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Compound-specific radiocarbon dating of lipid residues preserved in archaeological pottery vessels

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Abstract

While pottery vessels are widely recovered at archaeological sites their absolute dating by radiocarbon is challenging. Adsorbed lipids residues preserved within the matrix of the vessels and thus, protected from contamination in the burial environment, are widespread and often recovered in concentrations sufficient for radiocarbon dating. The most common residues correspond to animal fats, distinguishable by the dominance of the $C_{16:0}$ and $C_{18:0}$ fatty acids (FAs), have the potential to be dated at the molecular level using preparative capillary gas chromatography (PCGC; Stott *et al.* 2001; Berstan *et al.* 2008), however, the preliminary studies did not meet the accuracy and precision required. This thesis addressed the compound-specific radiocarbon analysis (CSRA) of adsorbed lipids extracted from pottery vessels for the establishment of a reliable procedure which can be used as routine.

The first consideration focussed on the elimination of exogenous contaminants associated with the isolation procedure. This consisted of (i) quantifying the contamination associated with the thermal degradation of the GC column stationary phase, which was demonstrated to be negligible, (ii) the elimination of the solvent used for recovery of trapped analytes using a new trap design, and (iii) the removal of 'memory' in the trapping system using a heat-based cleaning method. The accuracy and precision of ^{14}C determinations using PCGC were first established by dating bulk and isolated compounds on a wide age range of FAs from modern standards and archaeological bog butters prior to its application to 100 pottery vessels.

The ^{14}C dates on lipids extracted from pottery vessels showed excellent compatibility for dendrochronologically and radiocarbon dated materials from sites in wetland (Sweet Track, UK) and arid (Takarkori Rock Shelter, Libya) locations. The oldest dates obtained from the site of Çatalhöyük (Turkey) were successfully tested in the pre-existing Bayesian statistical model based on the stratigraphy. However, pot lipids from a coastal site (Cliffs End Farm, UK) produced older ages than their surface residues analogues probably due to a reservoir effect from aquatic product processing in the vessels.

The organic residue analysis (ORA) of *ca.* 900 potsherds from the Alsace (France) region provided insights into sampling strategies for pottery assemblage through recognition of the potsherds with the highest potential for CSRA, namely: (i) cooking pots with high lipid preservation, (ii) refitted potsherds to avoid residual/intrusive materials, and (iii) lipid extracts without aquatic biomarkers to avoid reservoir effect. Radiocarbon dates on Alsatian potsherds were compatible with the reference dates on bones and surface residues. The dates on Middle Neolithic potsherds were successfully included in the Bayesian statistical model based on the seriation and typological study of pottery assemblages in the region.

The technique showed its unique use to answer questions relating to the exploitation of food procurement practices, such as the emergence of dairying in central Europe, where the earliest dairy residues were directly dated to the late 53rd century BC. Furthermore, the analysis of lipid residues from a coastal site (Bornais, UK) with known use of aquatic products led to the correction of ^{14}C dates of lipid extracts using an estimate for the percentage of marine and terrestrial fats processed in potsherds together with an appropriate value for the local marine reservoir offset.

Significantly, vessels of diverse ages and burial environments can now be routinely and accurately dated from their adsorbed lipid residues (deriving from terrestrial or aquatic commodities) with equivalent precision to other commonly dated materials.

A pépé Marcel,

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Author’s declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's *Regulations and Code of Practice for Research Degree Programmes* and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

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Abbreviations

ABA	acid – base - acid
AD	*Anno Domini* (after Christ)
AGE	automated graphitization equipment
AMS	accelerator mass spectrometry
APAA	ω-(*o*-alkylphenyl)alkanoic acid
BC	before Christ
BORS	*Bischheim Occidental du Rhin Supérieur*
BP	before present
BSTFA	*N,O*-bis(trimethylsilyl)trifluoroacetamide
cal BC	calibrated before Christ
C	carbon
CHS	carbonate handling system
CSRA	compound-specific radiocarbon analysis
DAG	diacylglycerols
DCM	dichloromethane
DHYA	dihydroxy fatty acid
DIC	dissolved inorganic carbon
EA	elemental analyser
EA-IRMS	elemental analyser-isotope ratio mass spectrometry
EI	electron ionisation
EN	Early Norse
FA	fatty acid
FAME	fatty acid methyl ester
FID	flame ionisation detector
FRO	fresh reservoir offset
G-Trap	Gerstel-trap
GC	gas chromatography
GC-C-IRMS	gas chromatography-combustion-isotope ratio mass spectrometry
GC-MS	gas chromatography-mass spectrometry
GC/Q-TOFMS	gas chromatography/quadrupole-time of flight mass spectrometer
HPLC	high performance liquid chromatography
HTGC	high temperature gas chromatography
HTGC-MS	high temperature gas chromatography-mass spectrometry
IFA	isoprenoid fatty acid
IS	internal standard
LA	Lower Alsace
LBK	*Linearbandkeramik*
LIA	Late Iron Age
LN	Late Norse
LP	lactase persistence
MAG	monoacylglycerol
MICADAS	mini radiocarbon dating system
MRE	marine reservoir effect
MN	Middle Norse
MP	Middle Pastoral
NISP	number of identified specimens

NMR	nuclear magnetic resonance
ORA	organic residue analysis
OXA	oxalic acid
PCGC	preparative capillary-gas chromatography
PDMS	poly(dimethylsiloxane)
PFC	preparative fraction collector
PSP	pneumatic sample press
S-Trap	solventless trap
SD	standard deviation
SIM	selected ion monitoring
TAG	triaclylglycerol
TIC	total ion chromatogram
TLE	total lipid extract
TMTD	4,8,12-trimethyltridecanoic acid
TP	team Poznan
TW	trap-waste
UA	Upper Alsace

Archaeological sites and materials codes

APC	Apc-Berekalja I, Eastern Hungary, Hungary
BIS	Bischoffsheim “AFUA du Stade”, Alsace, France
BN	Bornais, South Uist, Scotland
CEF	Cliffs End Farm, Isle of Thanet, Kent, England
COL	Colmar “Route de Rouffach”, Alsace, France
CUI	Cuiry les Chaudardes “les Fontinettes”, Paris Basin, France
ENS	Ensisheim “Ratfeld”, Alsace, France
GEL	Geleen-Janskamperveld, Graetheide, Netherlands
IB	Irish Bog Butter, Ireland
KAR	Karwowo 1, West Pomerinia, Poland
KON	Konigshoven 14, North Rhine Westphalia, Germany
KOP	Kopydlowo 6, Greater Poland, Poland
LDW	Ludwinowo 7, Kuyavia, Poland
MAK	Maastricht Klinkers, Heeswater, Netherlands
ROS	Rosheim “Sainte-Odile & Rittergass”, “Laser, Mittelweg & Sandgrube”, Alsace, France
SAM	Samubru. Kenya
SIE	Sierentz “Sandgrube”, “Tiergarten”, Alsace, France
SW	Sweet Track, Somerset Levels, England
TAK	Takarkori Rock Shelter, Acacus Mountains, Libya
TP	Çatalhöyük East, “TP area”, Turkey

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Smyth, J., Berstan, R., **Casanova, E.**, McCormick, F., Mulhall, I., Sikora, M., Synnott, C. and Evershed, R.P. The bog butter phenomenon: four millennia of dairy surplus and deposition. Under review.

Chapter1.

Introduction

Chapter 1. Introduction

1.1 Archaeological pottery vessel and organic residues analysis

1.1.1 Origins and use of pottery vessels

1.1.1.1 Earliest pottery across the world

The world's oldest clay pottery vessels come from the Jomon pottery tradition in Japan (Odai Yamamoto, Sotogahama) and were radiocarbon dated, from food residues, at ca. 13,800 BP (Rice 1987; Aikens 1995; Nakamura *et al.* 2001). These were supplanted by the controversial Chinese pottery from Xianrendong Cave radiocarbon dated by charcoal samples ca. 20,000 BP (Wu *et al.* 2012), nonetheless the stratigraphy may have been disturbed and the earliest contexts with pottery securely radiocarbon dated were ca. 12,500 BP (Kuzmin 2013, 2015). The earliest centre for pottery in Russia dates ca. 13,000 BP with the Gromatukha culture (Siberia; O'Malley *et al.* 1999; Kuzmin 2002). In Northern Africa, the earliest evidence for pottery dates to ca. 9,600 BP (Ténéré, Niger) with the survival of a potter's comb. However, the first pottery were recovered in Africa at the site of Ounjougou (Mali) or in the Nile Valley dates to ca. 9,400 BP (Close 1995; Huysecom *et al.* 2009; Jesse 2010). In Anatolia, the earliest pottery was found at the site of Çatalhöyük (Turkey), dated to ca. 8,300 BP. This region is believed to be the centre for the appearance and intensification in production and spread of pottery across Europe and South Western Asia (Moore 1995; Bayliss *et al.* 2015). In the 'new world' it is suggested that pottery vessels were produced in Amazonia (shell midden groups) and Columbia (San Jacinto) starting at ca. 7,000 BP by semi-sedentary groups, and later in Mesoamerica at ca. 3,500 BP by sedentary groups (Mexico; Roosevelt *et al.* 1991, 1995; Clark and Gosser 1995).

Pottery therefore appears to have been an independent invention in various places worldwide, so the questions arise - how and for what purpose? Several theories exist as to how clay pottery vessels were invented, such as the accidental burning of clay or the imitation of natural vessels (Hoopes and Barnett 1995). One theory is that their first use was to make food more edible (cooking pots), e.g. possibly to detoxify plants and grains, allowing their consumption by humans (Arnold 1985). A second theory suggests that pottery vessels were used for prestige, ritual displays and social identity (decorated pots; Close 1995; Hayden 1995; Hoopes and Barnett 1995).

The adoption and use of pottery is believed to be highly correlated with the Neolithisation process and sedentarism, (i.e. shift from hunting-gathering to farming and food production; Rice 1987; Hoopes and Barnett 1995). The earliest dates for pottery production in the Far East suggest, however, it was an invention by hunter-gatherers long before the beginning of farming (Roosevelt 1995; Wu *et al.* 2012; Craig *et al.* 2013). As an example, it is suggested that, in Africa, pots were invented for prestige by hunter-gatherers, who then used them as cooking pots and they could be used also for storage and carriage of foodstuffs before the adoption to a less mobile lifestyle (Close 1995; Dunne *et al.* 2012, 2016). It should be noted that in such regions the hunter-gatherer traditions persisted until recently (e.g. Hart and Hart 1986) and therefore, invention of pottery by these groups may not be rare.

1.1.1.2 Function of archaeological pottery

Pottery vessels are widely recovered from archaeological sites either as complete forms, which are quite rare, or fragmented sherds. Sherds survive well as they are not prone to disintegration in burial environments. They have been extensively studied (shape, decoration etc) to understand vessel function, obtain information on the cultures associated with them (e.g.

technology, trade, rituals etc) and to establish relative chronologies (typological and seriation studies, Section 1.2; Renfrew and Bahn 1991).

The main function of pottery vessels is as a cooking utensil. Vessels can be used to store, cook and serve food (Rice 1987; Orton and Hughes 2014). The form of the pottery (bowls, jars, bottles etc) is often correlated with its function, e.g. cooking of solid food in bowls as opposed to liquid storage in narrow neck jars and jugs (Rice 1987). Occasionally, cooking vessels can be identified by carbonised food residues or the presence of black deposits of soot from the cooking (Longacre 1995). More refined vessels (decorated) are often hypothesised to be used as 'table dishes' or for ritual purposes (e.g. associated with human graves). Vessel specialisation, related to the form and decorations can also be determined by organic residue analysis (ORA, Section 1.1.2). Thus, the contexts pots are recovered from (house floor, lateral pit, grave), their form and organic residues give clues about their function and use.

1.1.2 Food residues in archaeological pottery vessels

1.1.2.1 Organic residues in archaeological pottery vessels

Organic residues from food processing survive in pots in three forms: (i) rarely, food can be preserved in situ as vessel fills, (ii) visible residues from food crusts, usually regarded as cooking failures, on the surface of the vessel, (iii) absorbed food residues into the vessel wall (Evershed 2008). Because of the porous nature of the ceramic material, lipidic components from food may be trapped and preserved within the vessel wall. Lipid residues are transferred to the vessel matrix mainly by the heating of the pot during food processing and are generally preferentially absorbed into the upper part of the vessel (Charters *et al.* 1993b, 1997; Stern *et al.* 2000). This aids preservation and limits their degradation by bacterial activities.

The first work on absorbed lipid was performed in the late '70s (Condamin *et al.* 1976) for the detection of oil in amphorae. Following this, major advances on the concept of ORA were performed '90s (e.g. Evershed *et al.* 1990, 1994, 1997; Heron *et al.* 1991, Heron and Evershed 1993; Charters *et al.* 1993b). These studies proved that a wide range of lipids, of diverse origins, protected from contamination in the burial environment in the clay matrix (Heron *et al.* 1991), are extractable and identifiable by the use of chromatographic and spectrometric techniques. The trapped residues, that are proof of pottery use, can be analysed and identified using appropriate sampling strategies, extraction methods and instruments (Evershed *et al.* 1990, 1994; Charters *et al.* 1993b; Copley *et al.* 2003; Correa-Ascencio and Evershed 2014). Organic residues analysis (ORA) has become a major source of information regarding vessel technology, paleodiet, trade and exchange and paleoenvironment (Roffet-Salque *et al.* 2017).

Most of the organic residues identified relate to commodities processed in the pots, however, they can also correspond to surface sealants, decoration or adhesive. For instance, birch bark tar was used as a sealant during the late Neolithic in Greece, and to repair a broken jar of the Roman era (Urem-Kotsou *et al.* 2002; Charters *et al.* 1993a). ORA can also determine vessel specialisation, for example, amphorae and 'ollas' used to produce alcoholic beverages at Teotihuacan (200-550 AD, Mexico; Correa-Ascencio *et al.* 2014), dairy products processed in 'saucepan pots' or jars, rather than bowls, during the British Iron Age (Copley *et al.* 2005b) and sieves used to make cheese during the Polish Neolithic (Salque *et al.* 2013).

The main application of ORA has been to reconstruct paleodiets and understand which commodities were used for the economy at a site, region or cultural group. For instance, in the Mesolithic of the British Isles, ORA along with other faunal and human remains, revealed that hunter-gatherers had an economy based on fish exploitation, which shifted abruptly to an economy based on dairy products with the earliest Neolithic farmers before a slow return to

fishing activity from the Bronze age to Viking records (Cramp *et al.* 2014b). In addition, the recovery of plant and animal products, which are not native to the region/country, can inform about mobility, trade and colonisation by past populations, e.g. triterpenoids, characteristics of tree species from the Mediterranean or south Arabia, recovered in Romano-British vessels from 3rd century AD denote connectivity with other parts of the world (Brettell *et al.* 2014). Finally, ORA analysis, especially stable isotope analysis, can give clues relating to the paleoenvironment and plant exploitation. Fruits, (e.g. palm fruits; Copley *et al.* 2001), vegetables, (e.g. cabbage; Evershed *et al.* 1991) or plants (Dunne *et al.* 2016) from temperate, arid or aquatic environments can be distinguished. The isotopic signal of animal products, such as dairy products, will differ between temperate and arid environment depending on the type of plants (C_3 or C_4) on which the ruminant animals grazed (Copley *et al.* 2003; Dunne *et al.* 2012). These lipids, originating from food substance, reflect past diet which are contemporaneous to the time of use of the pots, thus contain chronological information.

1.1.2.2 Biomarkers in lipid residue analysis

A wide range of techniques have been employed for the analysis of organic compounds in organic residues, including spectroscopic techniques (Infrared, Raman) for bulk information or chromatographic and spectrometric techniques (GC, GC-MS, HPLC, GC-C-IRMS) for information at the molecular level (Mills and White 1994). GC-MS is the most commonly used technique for the analysis of lipid residues preserved in potsherds because it allows the identification of the structures of biomolecular components (biomarkers), allowing the determination of the origin of organic remains, based on the presence of characteristic compounds (Philp and Oung 1988; Evershed 1993; 2008). A good biomarker survives in archaeological contexts or is the result of degradation of a compound that is "unique" and characteristic of only one source, or a restricted group of sources (Figure 1-1; Evershed 2008).

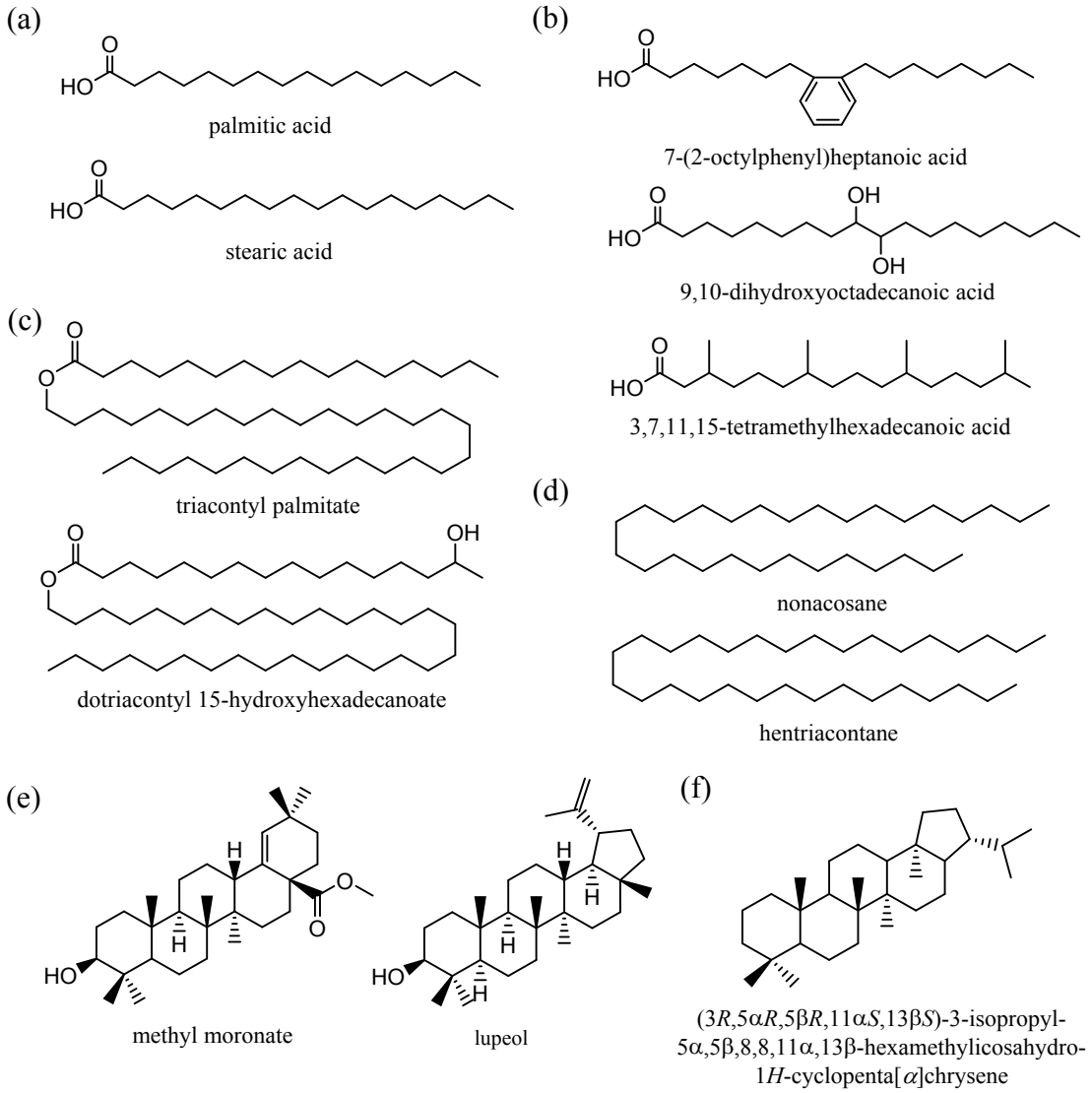

Figure 1-1: Main biomarkers used for the discrimination of (a) animal fats, (b) aquatic resources, (c) beeswax, (d) plants (e) resins, tars and (f) alcoholic beverage.

(i) Animal products are characterised by the high abundance of palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) fatty acids (FA; Figure 1-1a). Solvent extraction techniques can also reveal the presence of triglycerides (TAGs; Figure 1-2; Evershed *et al.* 1997, 2002a, 2002b; Correa-Ascencio and Evershed 2014). The distribution and abundance of the molecular components in the fresh fats differs according to their origin. For example, animal adipose fats contain TAGs, C_{42}-C_{54} for ruminant and C_{46}-C_{54} for porcine, and a narrow range of FAs ($C_{14:0}$-$C_{18:0}$; Evershed *et al.* 2002a; Mukherjee *et al.* 2005). Milk fats contain a lower molecular weight and wider range of TAGs between C_{24}-C_{54}, short

chain FAs ($C_{4:0}$-$C_{18:0}$) in addition to water, proteins and sugars (McCracken 1971b; Gresti *et al.* 1993; Dudd *et al.* 1998; Regert *et al.* 1998; Evershed *et al.* 2002a; Fontecha *et al.* 2005). In an archaeological context, the water-soluble fraction of organic residues dissolves and fatty components degrade by oxidation and hydrolysis (Mills and White 1994; Dudd *et al.* 1998; Evershed *et al.* 2002a; Correa-Ascencio and Evershed 2014). TAGs degrade by hydrolysis into diacylglycerols (DAGs) and monoacylglycerols (MAGs) by the loss of one or two FA moieties, thereby highly degraded fats contain primarily free fatty acids, with $C_{16:0}$ and $C_{18:0}$, as major components. Preferential losses of short chain fatty acids limits possibilities for discrimination between degraded adipose fats and milk fats based only on the presence and distribution of fatty acids and TAGs.

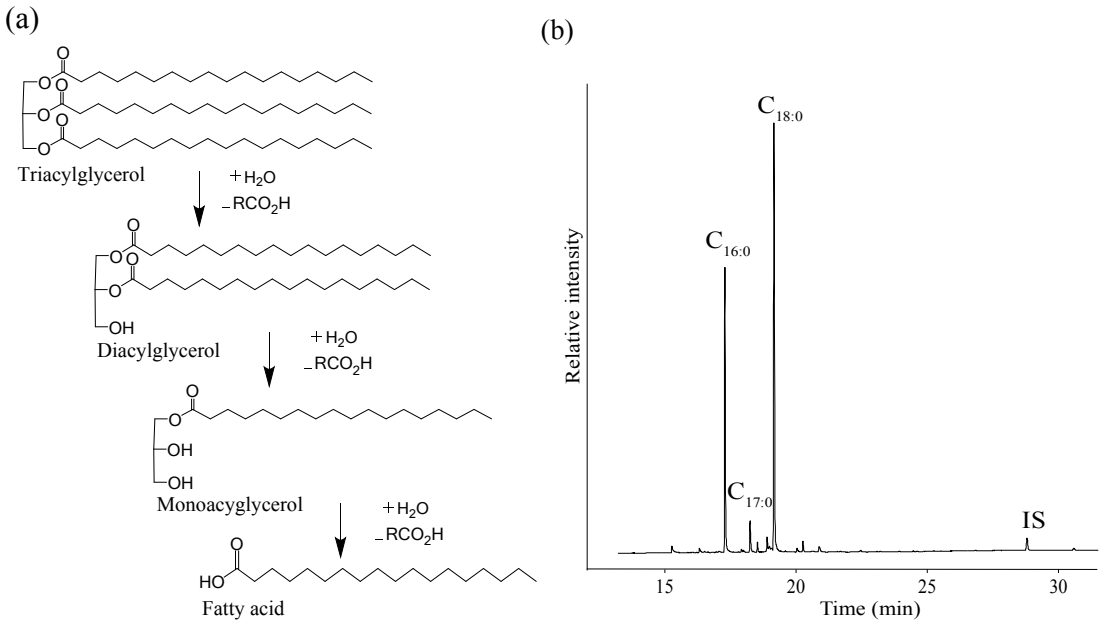

Figure 1-2: (a) Degradation of a triacylglycerol onto diacylglycerol and monoacylglycerol and fatty acids by hydrolysis (adapted from Evershed *et al.* 2002a). (b) Typical chromatogram of degraded animal fats characterised by the dominant of stearic and palmitic acids

(ii) Aquatic resources, such as terrestrial animal products, display high abundances of $C_{16:0}$ and $C_{18:0}$ FAs, however, they can be further discriminated in archaeological residues by

the presence of isoprenoid fatty acids (IFAs), vicinal dihydroxy acids (DHYAs) and ω-(o-alkylphenyl)alkanoic acids (APAAs; Figure 1-1b, 1-3; Hansel *et al.* 2004; Evershed *et al.* 2008a; Hansel and Evershed 2009; Cramp and Evershed 2014). The last two class of compounds are more stable than their precursor mono- and polyunsaturated fatty acids (PUFAs) present in fresh aquatic products, which are highly prone to degradation. The DHYAs result from the oxidation of monounsaturated FAs, whereas the APAAs result of the cyclisation of PUFAs through heating to > 270 ºC. Whereas the C_{18} DHYA, C_{18} APAA and the phytanic acid can be recovered in terrestrial organisms the C_{20} and C_{22} DHYAs and APAAS as well as the 4,8,12-trimethyltridecanoic acid (TMTD; IFA) are only formed from fats and oils derived from aquatic organisms and, therefore, can be used as biomarker proxies for the exploitation and processing of such resources by past populations.

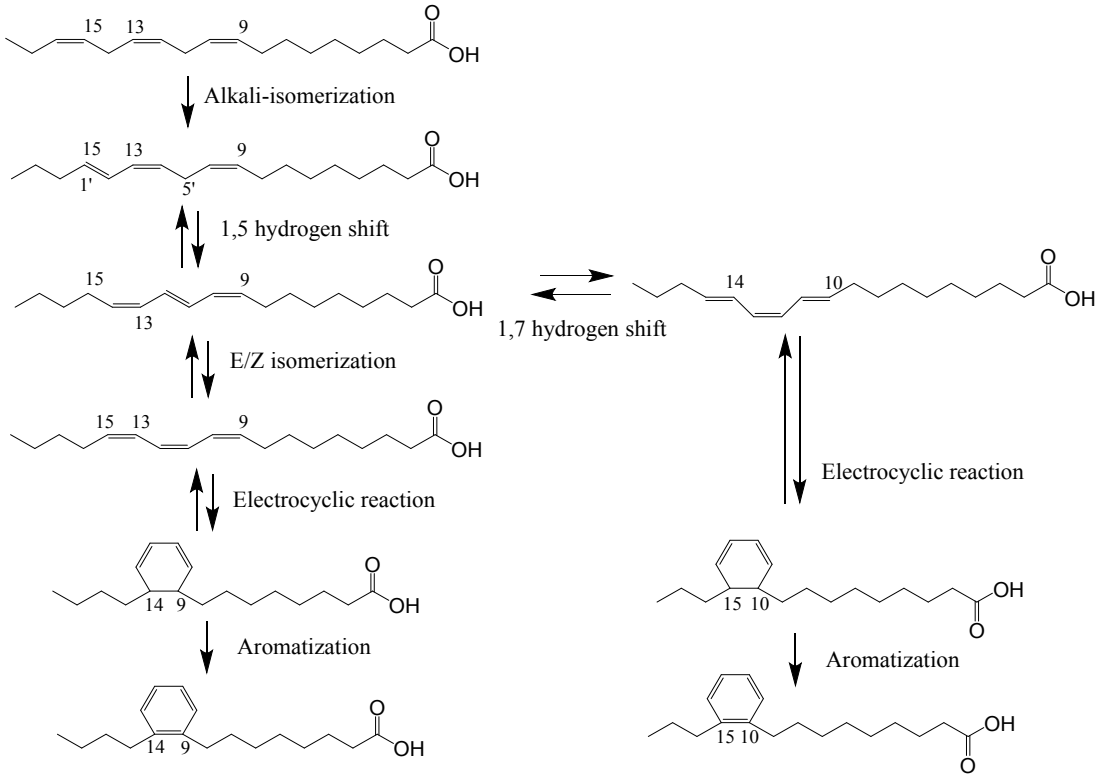

Figure 1-3: Formation of ω-(o-alkylphenyl)alkanoic acids, adapted from Hansel *et al.* (2004).

(iii) Beeswax is characterized by, alkyl palmitate monoesters (from C_{38}-C_{52}), hydroxy palmitate monoesters (with long chain alcohol C_{24}-C_{38}), alkanoic acids (C_{20}-C_{36}) and a range of odd-numbered alkanes and alkenes from C_{23} to C_{31} dominated by the C_{27}. The monoesters are resistant to degradation due to their hydrophobicity and are used as diagnostic biomarkers for beeswax (Figure 1-1c). When the waxes esters are hydrolysed, as is commonplace in archaeological residues, beeswax is recognised by presence of free palmitic acid and a series of free *n*-alkanols (C_{20}-$C_{32;}$ Charters *et al.* 1995; Regert *et al.* 2001; Correa-Ascencio and Evershed 2014).

(iv) Plant residues can be identified archaeologically by the presence of short (C_9) and long chain (up to C_{31}) FAs, the former resulting from the oxidation of unsaturated FAs. Cuticular wax derived *n*-alkanes with distributions from C_{25}-C_{31} serve as indicators for processing of leafy vegetables. Discriminating between plant type can be achieved by considering the *n*-alkane distributions, such as the dominance of C_{23} and C_{25} for aquatic plants, or the dominance of longer-chain alkanes up to C_{30} for leafy vegetables, whereas C_3 or C_4 wild grasses and sedges are dominated by the C_{31} homologue (Figure 1-1d; Evershed *et al.* 1991; Dunne *et al.* 2016).

(v) Residues of plant resins display characteristic terpenoid biomarker compositions allowing their biological origins often to be defined at high taxonomic specificity (Figure 1-1e). For instance specific di- and triterpenic compounds are used to identify resins, pitch and tars, e.g. methyl dehydroabietate for coniferous resin, methyl moronate and methyl oleanoate for *Pistacia* resins (Stern *et al.* 2003) and lupeol, lupenone and betulin for birch bark tar (Bosquet *et al.* 2001; Urem-Kotsou *et al.* 2002).

(vi) A variety of other biomarkers are used to identify less common residues found in archaeological pottery, e.g. palm fruit is identified by high concentrations of $C_{12:0}$ and $C_{14:0}$ FAs (Copley *et al.* 2001), and a bacterially fermented alcoholic beverage were identified by the presence of hopanoids (Figure 1-1f; Correa-Ascencio *et al.* 2014).

1.1.2.3 Stable isotope analysis in organic residue analysis

1.1.2.3.1 Principles of stable isotope analysis

The introduction of compound-specific stable isotope analysis by gas chromatography–combustion–isotope ratio mass spectrometry (GC-C-IRMS) provided a step change in the study of organic residues offer valuable information about past diet and food procurement practices (Evershed *et al.* 1994, 1997; Evershed 2009). This technique measures the ratio of the stable isotopes of an element. For carbon, the ratio $R = {}^{13}C/{}^{12}C$ is normalised against the Vienna Peedee Belemnite standard which are reported as a $\delta^{13}C$ value ($= R_{sample}/R_{standard} - 1$) expressed in per mil. The stable carbon isotope compositions of compounds in biological tissues vary characteristically between different organisms due to trophic levels and fractionation effects during biochemical reactions.

Each living organism contains a variable proportion of the stable isotopes of an element due to the preferential incorporation of one isotope over the other ones during chemical, biological or physical processes or during isotope exchange leading to an equilibrium state. This phenomenon is known as fractionation. The relative abundances of stable isotope of an element, can provide distinctive signatures for biologic materials and has use as an environmental tracer (Schoeller 1999; Evershed 1999). For instance, terrestrial plants vary in their carbon isotope composition due them possessing different mechanism of photosynthesis (i.e. CO_2 fixation), such that C_3 (temperate environment) can be distinguished isotopically from

C_4 (arid environments), with aquatic plants overlapping with C_4 (O'Leary 1981). These differences are of particular interest when considering trophic interactions (by looking at $\delta^{15}N$ values), where food from a lower (e.g. plants) or a higher trophic level (e.g. meat), is ingested by other organisms (e.g. humans or domesticated animals); the exact food or combination of food will influence the carbon isotope signal of the consumer organism based on the "*you are what you eat (assimilate)*" principle (Figure 1-4; Evershed 1999).

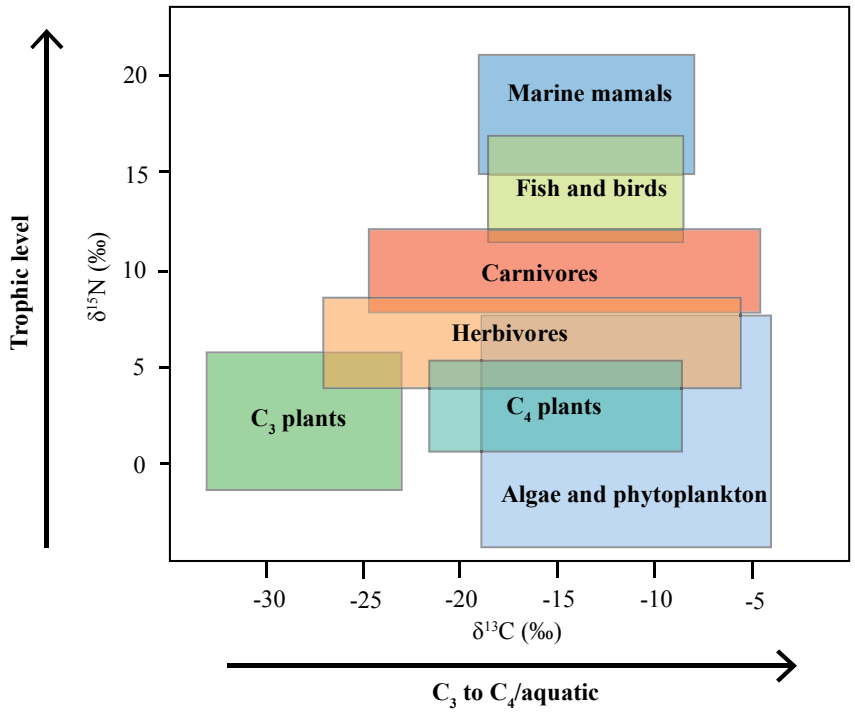

Figure 1-4: $\delta^{15}N$ plotted against $\delta^{13}C$ isotope to increasing trophic levels and increasing C_4/aquatic plants. Adapted from O'Connell (1996).

1.1.2.3.2 Use of stable isotope in lipid residue analysis

The use of stable carbon isotope analysis is now widely performed on lipids from pottery vessels. This includes recording of $\delta^{13}C$ values on *n*-alkanes to distinguish between C_3 and C_4 plants, related to a temperate or arid environment (Evershed *et al.* 1994; Dunne *et al.* 2016) and recording $\delta^{13}C$ values of fatty acids to distinguish the source of animal products (Evershed *et al.* 1997; Copley *et al.* 2003; Cramp and Evershed 2014).

A proxy based on $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ FAs proved efficient to discriminate ruminant adipose products from non-ruminant adipose products and ruminant dairy products due to their different metabolism (Figure 1-5; Evershed *et al.* 1997, 2002a; Dudd and Evershed 1998; Copley *et al.* 2003). Such criterion was first applied on Medieval vessels with the recognition that lamps contained ruminant products and dripping dishes contained pig products based on the observation that $\delta^{13}C$ values from pig adipose fats were more enriched than fats from cattle/sheep/goat (Evershed *et al.* 1997). This proxy has become a key tool for identifying dairy products which have $\delta^{13}C_{18:0}$ values more depleted than adipose fats due to the $C_{18:0}$ originating from the diet (via biohydrogenation of unsaturated fatty acids) as opposed to the $C_{16:0}$ which is produced biosynthetically by the animals mammary glands (Dudd and Evershed 1998; Copley *et al.* 2003, 2005a).

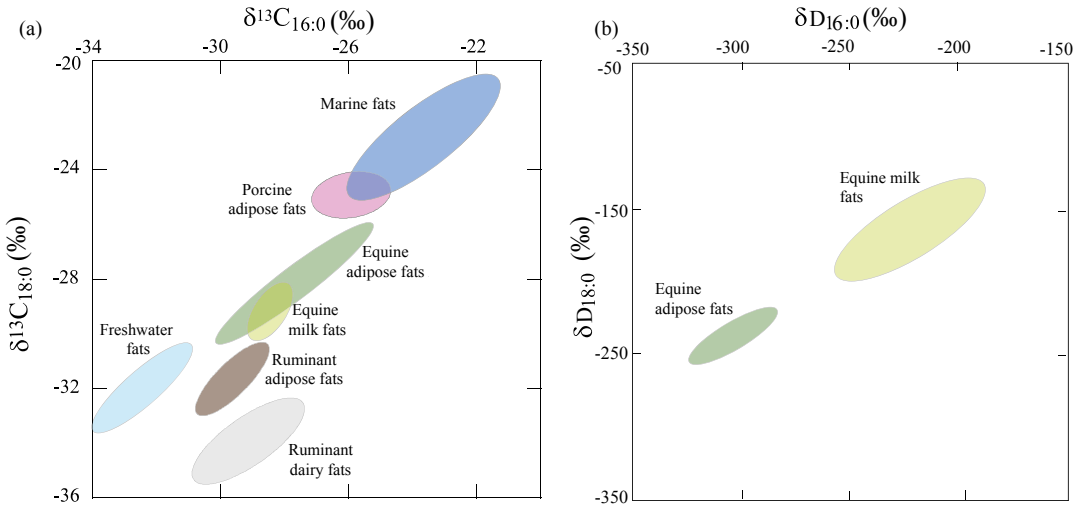

Figure 1-5: (a) Reference ellipses of $\delta^{13}C_{18:0}$ plotted against $\delta^{13}C_{16:0}$ for ruminant adipose, non-ruminant adipose, ruminant dairy, equine adipose, equine milk, freshwater and marine fats from reference animals (from Copley *et al.* 2003, Outram *et al.* 2009 and Cramp and Evershed 2014). (b) Reference ellipses of $\delta DC_{18:0}$ plotted against $\delta DC_{16:0}$ for equine adipose and milk fats (from Outram *et al.* 2009).

The first reference animals (cattle, sheep goat and pigs) raised on a pure C_3 diet came from the UK (Copley *et al.* 2003). Typically, when the $\delta^{13}C_{18:0}$ values are plotted against the $\delta^{13}C_{16:0}$ values for one TLE, fall within the reference ellipses (68 % of the reference values; Figure 1-6a) of modern animal products (e.g. dairy), animal fats can be assigned to the particular

source (Copley *et al.* 2003). If these are just outside one reference ellipse these can be considered as dominated by one animal product. If the $\delta^{13}C$ values plot between two reference ellipses (e.g. dairy and non-ruminant adipose fats) along the mixing lines (Figure 1-6a) it is considered as being the result of the mixing of two sources of fats (Mukherjee *et al.* 2005). Later it has been shown that raising animal on a C_4 diet (often evidence for a more arid environment) shift ruminant animal products of cattle and caprines outside the reference ellipses of animals raised on C_3 diet similarly to mixing with non-ruminant products (Figure 1-6; Copley *et al.* 2005c; Dunne *et al.* 2012). This environmental effect is removed with $\Delta^{13}C$ (= $\delta^{13}C_{18:0}$ - $\delta^{13}C_{16:0}$) values plotted against $\delta^{13}C_{16:0}$ values (Figure 1-6b). With this representation dairy residues dominate the TLE with $\Delta^{13}C$ values below -3.1 ‰ (Copley *et al.* 2004; Dunne *et al.* 2012). Typically, a ruminant carcass product signal is detected when $\Delta^{13}C$ values are between -3.1‰ and 0.3 ‰ and non-ruminant adipose signal when values are above 0.3 ‰. This representation is nonetheless not as useful in the case of mixtures of two animal products as a false positive signal would appear in the ruminant adipose fat region. The joint use of both proxies is, therefore, necessary to understand if the $\delta^{13}C$ values could be affected by a mixture of two animal products or an environmental effect.

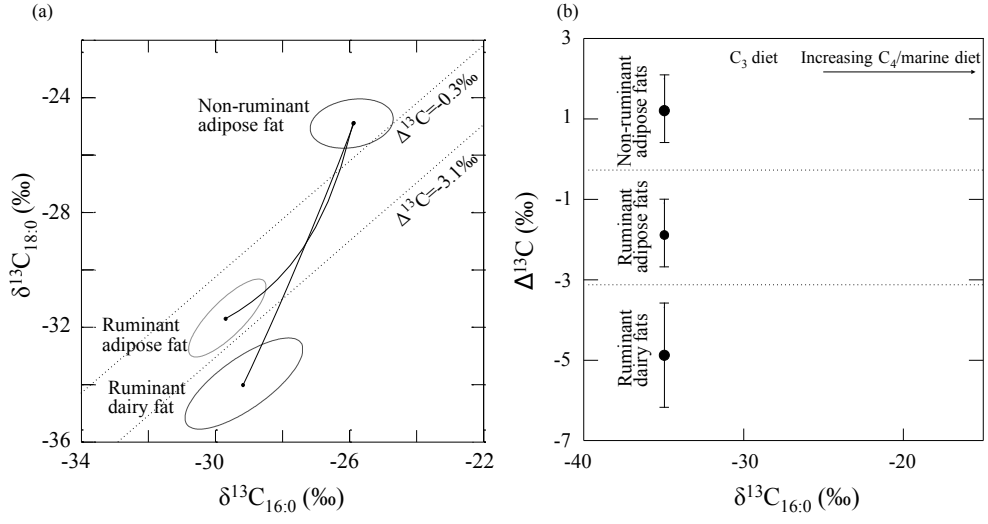

Figure 1-6: (a) Reference ellipses of $\delta^{13}C_{18:0}$ plotted against $\delta^{13}C_{16:0}$ for ruminant adipose, non-ruminant adipose, ruminant dairy and mixing lines. (b) $\Delta^{13}C$ values plotted against $\delta^{13}C_{16:0}$ values and influence of C_4/marine diet.

Equine products would typically fall within the mixing lines between cattle/caprines and porcine products (Figure 1-5a). Equine milk cannot be distinguished from equine adipose fat based on fatty acid $\delta^{13}C$ values. However, separation of these two horse products was achieved based on the δD values (Figure 1-5b), on the same FAs, which vary with the season of production, i.e. year round (for adipose) *versus* late spring/summer (for milk); this allowed horse milking to be recognised at 3,500 BC in Kazakhstan providing crucial evidence for early horse domestication (Outram *et al.* 2009, 2012).

The proxy also allows the fats of marine organisms to be distinguished from terrestrial organisms through the more enriched $\delta^{13}C$ values of the former (Figure 1-5a; Cramp and Evershed 2014). This is due a ca. 7 ‰ enrichment of oceans bicarbonates related atmospheric CO_2 that gives phytoplankton, and consequently organisms from higher trophic level feeding from them, enriched values (Chisholm *et al.* 1982). Furthermore, the $\delta^{13}C$ values from individual FAs similar or more enriched than the $\delta^{13}C$ values of the non-ruminant adipose fat ellipse suggest the use of marine products (Cramp and Evershed 2014). In the $\Delta^{13}C$ representation, this would overlap with non-ruminant products but would be shifted to enriched values similarly to a C_4 diet (Figure 1-6b).

Freshwater organisms, however, have usually more depleted $\delta^{13}C$ values due to the contribution of degraded terrestrial matter, which is isotopically depleted, to lake and river C cycles (Dufour *et al.* 1999). This input of terrestrial matter would, however, variate between freshwater bodies (Dufour *et al.* 1999). Also, organic residues giving $\Delta^{13}C$ values above -0.3 ‰ are considered to come from non-ruminant products (or marine products) but such values, together with depleted $\delta^{13}C_{16:0}$ values ranging between -31 and -37 ‰ (for UK and Kazakhstan references), would suggest the processing of freshwater organisms (Cramp and Evershed 2014).

The possibility of using FAs $\delta^{13}C$ values is of particular importance at archaeological sites from coastal areas when aquatic biomarkers in pottery are not detectable. The proxies presented in Figure 1-6 are used jointly to understand the local diet, mixing of animal products and environmental effect at a particular site. The use of such proxy can also benefit from faunal assemblages to identify animal species present at the site to narrow down the possible sources of animal fats.

1.2 Dating of pottery vessels

A summary of the methods used to date pottery vessels are given in Table 1-1.

Table 1-1: Dating techniques for pottery vessels, principle, benefits and limitations.

Technique	Principle	Benefits	Limitations
Stratigraphy	- Pottery compared to artefacts in a sequence	- non-destructive - contemporaneity of artefacts of different nature	- relative age - intrusive/residual materials - site study only
Typological sequence & seriation	- Look at typological similarities, evolution and frequency of pottery	- non-destructive - frequency of typological characteristics - tight chronologies	- relative age - regional studies only
Archaeomagnetic dating	- Date the manufacture or last firing of pottery based on the orientation or intensity of magnetic field	- non-destructive - no reservoir/old wood effect	- relative age - not-precise - demagnetisation of pottery prior to dating - limited to materials preserved in the kiln - fired clay pots
Thermoluminescence dating (TL)	- Date the manufacture of the pottery based on the energy accumulated after firing	- absolute age - no reservoir/old wood effect - possibility to convert into a calendar age	- not-precise - second heating of pottery - clay with mineral inclusions only - inefficient original firing - no TL signal
Rehydroxylation dating	- Date of the manufacture of the pottery based on kinetic law of clay combination with moisture	- no reservoir/old wood effect - calendar age	- slow kinetic reaction - second heating of pottery – temperature influence - mass addition by the temper
Radiocarbon dating (^{14}C)	- Date of the manufacture (temper, soot) or the use of the pottery (organic resides) by measuring their ^{14}C content	- absolute age - precise - possibility to convert into a calendar age	- destructive - exogenous contaminants - reservoir/old wood effect - no organic residues or temper survival

1.2.1 Relative dating of pottery at site and regional scale

1.2.1.1 Stratigraphy

The earliest archaeological technique used to relative date artefacts and introduced by Nicolas Steno in the XVIIth century (Steno 1669; Harris 1989) is stratigraphy. Stratigraphy is based on the hypothesis that (at a site) contemporaneity occurs horizontally (1 layer) in space, and variations through time occur vertically (1 sequence; Steno 1669; Harris 1989; Lyell 1990). Over time, layers are deposited one above another, thus, the surface layer corresponds to the youngest and the bottom layer to the oldest. Within one layer the artefacts, human and faunal remains recovered are contemporaneous and relatively younger than the layers below and older than the layers above (Steno 1669; Harris 1989; Lyell 1990). If one artefact from a layer can be radiocarbon dated, then the whole layer (if considered homogeneous) is dated, therefore, pottery can be dated indirectly via other materials. Sometimes the stratigraphy has been disturbed, thus a material from a previous phase recovered in a younger layer is known as residual material, while a younger material in an older layer is known as intrusive material (Renfrew and Bahn 1991). This relative technique is limited to the site scale and does not yield calendrical dates.

1.2.1.2 Typological sequence and seriation

Pottery vessels can be relatively ordered in chronological sequences by their visual characteristics (Renfrew and Bahn 1991; Rice 1987). Earliest structural and typological observations originated from Christian Thomsen, who established the Three-Age System recognising the relative chronology of Stone, Bronze then Iron Age by the nature of artefacts recovered at sites (Gräslund 1987). Sequence dating is based on grouping artefacts according to the similarities in their typology (i.e. style, decoration, shape or size). In practice, the

frequency of typological criteria for a certain period is looked at, as the characteristics of artefacts gradually change through time. Some attributes, like the decoration of pottery, can change faster than the shape because this latter attribute can be influenced by its function. Therefore, short-term change attributes are preferentially used for typological and seriation studies (Dunnell 1970). Seriation studies focus on the organisation of assemblages of artefacts in series based on their typological criteria (Dunnell 1970). Contrary to stratigraphy, seriations are often regional studies of the same cultural tradition as no spatial scale uniformity is possible through the ages (Dunnell 1970; Renfrew and Bahn 1991). Seriation only investigates the variation in time (rather than the variation in space) to build precise relative chronologies; however, no calendar age can be precisely deduced (Dunnell 1970; Renfrew and Bahn 1991).

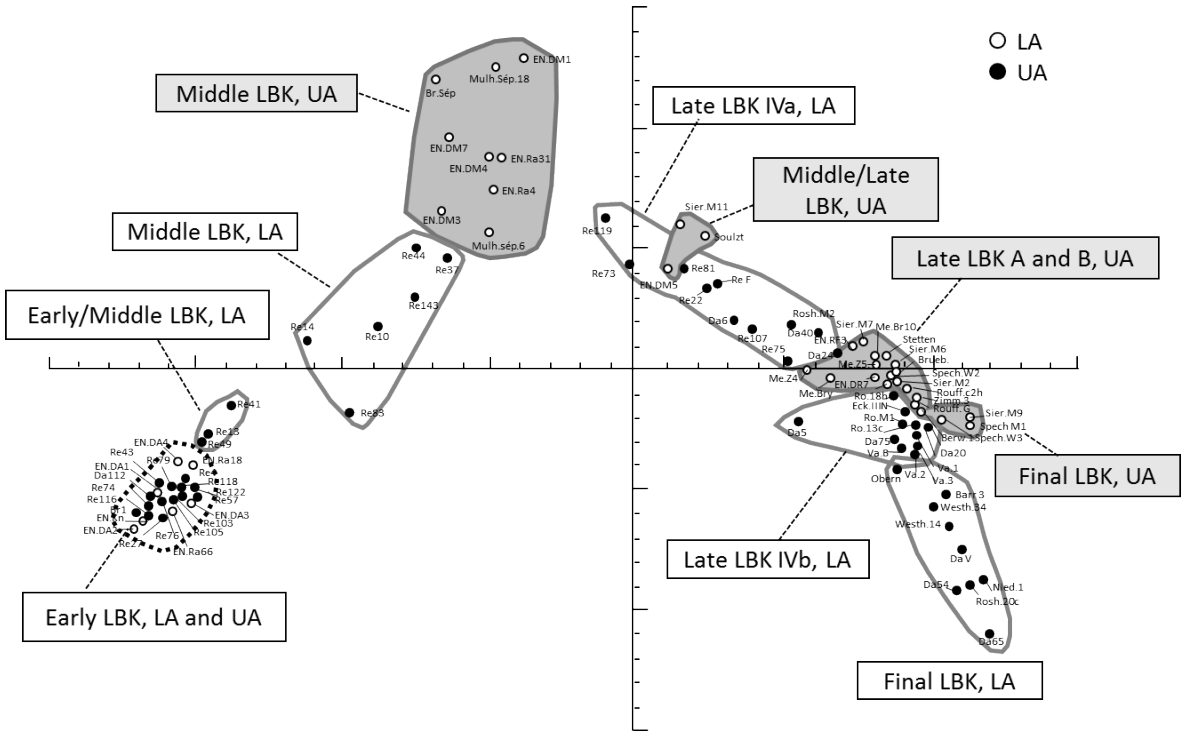

Figure 1-7: Correspondence analysis of the early Neolithic groups (LBK) in the Lower and Upper Alsace and definition of the chronological steps. Adapted from Lefranc (2007, Figure 29).

The pioneering work on seriation was performed in the 19th century by Sir William F. Petrie who organized cemetery graves based on the form of pottery associated with them (Renfrew

and Bahn 1991). Following this work mathematics (matrices and correspondence analysis) emerged as a tool to help with the discrimination of the artefacts by considering their principal constituents (Hole and Shaw 1967; Kendall 1970; Bolviken *et al.* 1982). Examples of regional seriation studies have been performed for Neolithic assemblages in the Alsace region (France) which were distinguished, by typology, the successive cultural groups and also determined two subgroups and 5 phases for the earliest Neolithic culture (Lefranc 2007; Denaire 2009a). Decorative pottery was separated by correspondence analysis, based on the main and secondary decorative motifs and motif on the rims (Figure 1-7; Lefranc 2007).

1.2.2 Archaeomagnetic, thermoluminescence and rehydroxylation dating

In broad terms, archaeomagnetic, thermoluminescence and rehydroxylation dating are based on the storage of information on the manufacturing time of a pot in the clay matrix (Aitken 1970). Clay contains ferrimagnetic minerals with a disorganised magnetic moment. During the firing of the pot thermal agitation means the grains in the clay magnetise orientating with the Earth's magnetic field. This orientation remains in place (thermoremanent magnetism) once the pot is cooled (Aitken 1970). Measuring the direction of the magnetic moment associated with the pottery allows it to be dated. Magnetic dating is, however, limited to periods which show a significant change in the Earth's magnetic field and requires regional reference curves built from known age artefacts to convert it into a calendar age (Aitken 1970). The technique is mainly employed to date the last use of kilns by their bricks and remaining pottery *in situ*. Pottery which has been moved from the kiln after firing does not give satisfactory results, as the orientation when the cooling occurred is not accurately known (Aitken 1970; Rice 1987). For such material, the intensity (proportional to the Earth's magnetic field at a given time) rather than the direction, can be measured (Bucha 1970). In such cases, the thermoremanent magnetism is measured, before and after heating of the pottery above 600 ºC allowing the ratio

of the past to present magnetic fields to be obtained which can be related to historical event using reference curves.

Thermoluminescence dating involves measuring the accumulation of energy from cosmic radiation in the crystalline part of pottery since firing, i.e. manufacture (Aitken 1970). The crystalline materials (e.g. quartz) accumulate energy from natural radiation, however, heating above 500 ºC allows the release of this energy, thus, during the manufacture of the pot the crystals are reset to their initial state and start reaccumulating energy (Aitken 1970). The thermoluminescence analysis by rapid heating of the pottery allows to obtain to the age of the pot, in practice, however, many measurements need to be taken into account for a precise dating (Aitken 1990). This technique is limited to pots fired once at high temperature which cooled down in the kiln (Rice 1987; Aitken 1990). Both archaeomagnetic and thermoluminescence dating are significantly less sensitive and thus less precise than radiocarbon determinations (Aitken 1990).

Rehydroxylation dating technique, based on the combination of clay -OH groups with ambient moisture after firing, was introduced in the 21^{rst} Century (Wilson *et al.* 2009; Wilson *et al.* 2012). This technique allows to date events based on gravimetry as the mass of a pottery increases in contact with moisture following kinetic laws (Wilson *et al.* 2009). In practice a piece of a potsherd is dehydrated, and the mass loss recorded before recombination with ambient moisture to measure the kinetic rate for hydroxylation (Wilson *et al.* 2012). This allows measuring when the firing event occurred. The technique is, however, temperature sensitive (Hall *et al.* 2013) and limited to potsherds that have been fired once. The method has also proven challenging for archaeological pottery containing inclusions/temper biasing the mass loss/uptake during the measurement (e.g. Shoval and Paz 2013; Burakov and Nachasova 2013).

1.2.3 Radiocarbon dating pottery vessels

1.2.3.1 Sources of carbon in pottery vessels

Archaeological pottery vessels can be radiocarbon dated (principles explained Section 1.3) if a source of carbon contemporaneous to their manufacture or their use is available. There are a number of sources of carbon associated with archaeological pottery (de Atley 1980; Gabasio *et al.* 1986) and could be radiocarbon dated:

(i) The carbon from the clay which will vary depending on the source of the clay (Gabasio *et al.* 1986). This fraction will give a date older than its manufacture as it will be contemporaneous to the clay formation.

(ii) The carbon from temper (e.g. shell, vegetable matter) which is usually contemporaneous to the manufacture of the pot (Gabasio *et al.* 1986). Dating this fraction can give good results, but it requires the temper to be organic (for short lived materials contemporaneous to the manufacture, Section 1.3.3.1), and survive the firing.

(iii) The carbon from the fuel in the kiln may be contemporaneous with the manufacture or use of the pots (Gabasio *et al.* 1986), however, this can be prone to the "old wood effect" (see Section 1.3.3.1) if older wood, was used in firing. In addition, such residues appear on the outer walls of vessels as soot, could also arise from fuel used to heat pots during cooking and burnt food residues (Teetaert *et al.* 2017).

(iv) The carbon from the use of the pottery, i.e. food residues from cooking or storage of organic commodities that are contemporaneous to the use of vessels (Gabasio *et al.* 1986). Two types are present, the visible or charred residues and the residues absorbed in the clay matrix. Commonly, charred (surface) residues are dated (Brock *et al.* 2010),

however, direct contact of these residues with the burial environment means they are highly prone to contamination, which is difficult to identify and quantify prior to dating. Furthermore, such residues are quite "rare" in an archaeological context. These contrast with the invisible absorbed residues, which are preserved within the clay matrix and less prone to contamination but are largely untapped for ^{14}C dating.

1.2.3.2 History of radiocarbon dating pottery vessels

Early attempts at radiocarbon dating pottery vessels, either from their temper or visible organic residues, were reported in the 1960's, however, they did not necessarily come from securely dated contexts, thereby failing to meet the rigor required for evaluating protocols (Stuckenrath 1963; Engstrand 1965; Tauber 1968; Taylor and Berger 1968). The first dates on the clay of pottery vessels used kilograms of sherds for one ^{14}C age determination by decay counting (de Atley 1980), which, would never have feasible as a routine method before the introduction of AMS technology (see Section 1.3.2). The difficulty of dating potsherd was immediately revealed with reproducibility and consistency of dates being difficult to achieve, probably due to the uncertainties surrounding the sources of carbon in pottery (de Atley 1980).

Gabasio *et al.* (1986) and Evin *et al.* (1989), simulated Neolithic pottery manufacture for the isolation of the clay, temper and carbon from the fuel, prior to its application to archaeological pots, which highlighted the fuel as the best fraction for dating but the results were irreproducible. Johnson *et al.* (1986) achieved the isolation of carbonised residues from the clay and compared the radiocarbon and thermoluminescence dates; this constituted the first rigorous testing of the method. Hedges *et al.* (1992) focussed on isolating and dating the different carbon fractions and obtained reproducible results on the temper, promising results on the surface residues and clay. However, the lipids fraction gave highly irreproducible results

likely due to contamination during extraction. Delqué Kolic (1995), focused on dating the soot residues, and the reproducibility obtained with modern reference samples was not achieved with the archaeological potsherds, probably due to contamination within the burial environment. The dating at the molecular level of lipids preserved within the clay attempted by Stott *et al.* (2001, 2003) achieved significant progress in the purification of the lipid fraction prior to ^{14}C dating, however, the date obtained lacked the accuracy required for use in archaeology by up to 500 years (with both older and younger ages).

In summary, most recent attempts at radiocarbon dating pottery vessels have focussed on the organic temper (e.g. Gomes and Vega 1999; O'Malley *et al.* 1999; Mihara *et al.* 2004; Yoshida *et al.* 2004; Messili *et al.* 2013) or on charred residues (e.g. Nakamura *et al.* 2001; McKinley *et al.* 2014). These are however limited to (i) the survival of such a C fraction which can be lost during firing and cooking events, and (ii) their effective separation from exogenous C to allow dating of events contemporaneous to the manufacture/use of the potsherd only.

Therefore, the radiocarbon dating of pottery vessels is limited to the survival of temper and surface residue and are not performed as routine but done when no other material is datable.

1.3 Fundamentals in radiocarbon dating

1.3.1 The radionuclide and distribution in the biosphere

1.3.1.1 The stable isotope of carbon and the radionuclide

Carbon has two stable isotopes, ^{12}C and ^{13}C, with natural abundances of 98.89 % and 1.11 % respectively (Schoeller 1999), and one unstable isotope ^{14}C (radiocarbon or radionuclide) found in abundances at one part per trillion (ppt). The naturally occurring radioactive isotope of carbon, is formed in the upper atmosphere by the interaction of ^{14}N atoms and the neutrons

produced by cosmic radiation (Anderson *et al.* 1947; Korf and Mendell 1980). The radiocarbon rapidly oxidises to ^{14}CO and $^{14}CO_2$ mixes with the atmosphere, then enters into the biosynthesis of the biosphere and dissolves in aquatic environments (Figure 1-8; Anderson 1953; Craig 1957; Aitken 1990).

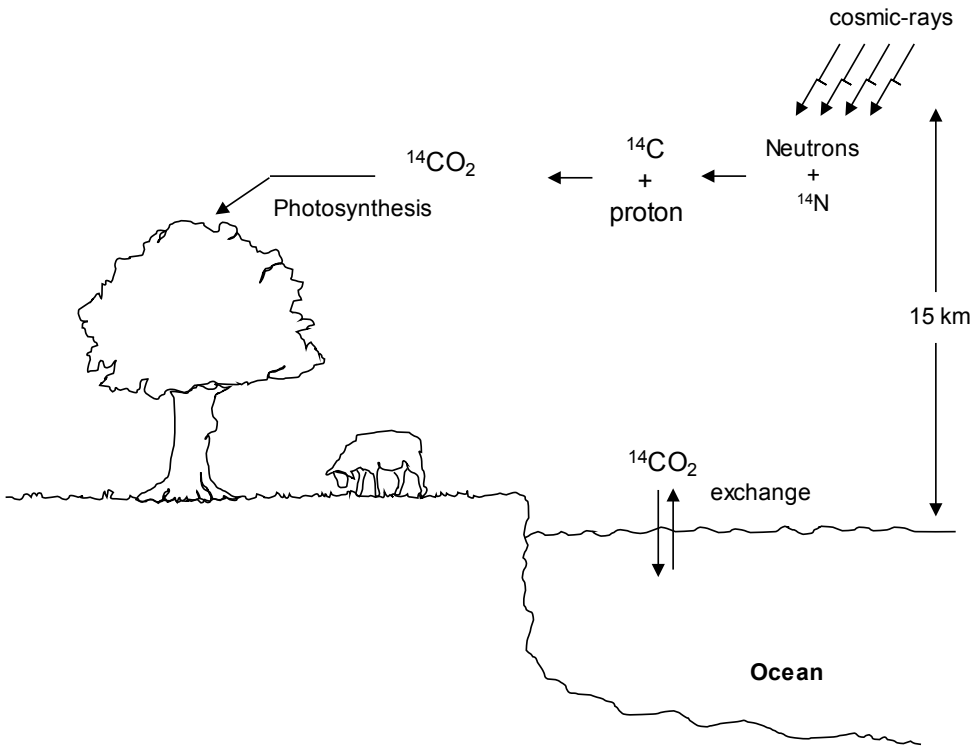

Figure 1-8: Radiocarbon formation in the upper atmosphere and mixing in the biosphere. Adapted from Aitken (1990, Figure 3.1).

Relative abundance of isotope of an element varies between the reservoirs (sites where C is stored e.g. atmosphere, ocean or biosphere) in given environments (Schoeller 1999; Section 1.1.2.3.1). An organism, during its lifetime, rapidly exchange ^{14}C with the surrunding environment (Anderson 1953; Bowman 1990). After the death of the organism, there is no more exchange of ^{14}C with the exterior, i.e. it is a closed system, and its ^{14}C content starts decreasing at an exponential rate due to radioactive decay (Bowman 1990; Equation 1-1). The activity of a sample is defined as the number of decays per time and mass units, expressed in $Bq.kg^{1}$ of C (SI) and is proportional to the number of ^{14}C atoms.

$$A = A_0 e^{-\lambda t}$$

Equation 1-1

Where A = activity after the time t (SI)
A_0 = initial activity at the time of death (SI)
λ = mean life of radiocarbon (i.e. $\ln(2)/T_{1/2} = 8033$ (y))
t = radiocarbon age (y)

The natural decay of this radioisotope is used extensively as a dating technique for archaeological events (Aitken 1990). The half-life of radiocarbon, $T_{1/2}$, defined as the time it takes for half an amount of ^{14}C atoms to decay, is of 5,730 ± 40 years (Godwin 1962). So, by determining the remaining proportion of the ^{14}C within an organism at the time it died can be calculated (Libby *et al.* 1949; Arnold and Libby 1949). In practice, for historical reasons, the Libby half-life of 5,568 years is used to calculate the 'age' of an organism in radiocarbon years. The radiocarbon age of an organism can be calculated with the Equation 1-2 (rearranged form of the first order decay equation):

$$t = \lambda * \ln\left(\frac{A_0}{A}\right)$$

Equation 1-2

Where t = radiocarbon age (y)
λ = mean life of radiocarbon (y)
A_0 = initial activity at the time of death (SI)
A = residual activity after the time t (SI)

The approximate limit of detection time of radiocarbon is 50,000 years. Beyond this, there is no detectable ^{14}C which is referred as infinite age carbon, radiocarbon dead or fossil carbon (Taylor 1987).

Fractionation effects, occurring during the incorporation of atmospheric ^{14}C by an organism can be corrected when ^{14}C dating using $\delta^{13}C$ values which are stable over time. It involves normalising the activity of a material as if it was a wood sample ($\delta^{13}C$ = -25 ‰; Equation 1-3).

$$A_s = A_m * \left[\frac{1 + \delta^{13}C_w/1000}{1 + \delta^{13}C_s/1000}\right]^2$$

Equation 1-3

Where A_s = sample activity (SI)
A_m = measured activity (SI)
$\delta^{13}C_w$ = typical $\delta^{13}C$ value of a wood sample (= -25 ‰)
$\delta^{13}Cs$ = $\delta^{13}C$ value of the sample (‰)

However, the mixing rate in the different reservoirs of the biosphere and oceans are an issue as they can result in a significant difference in the ^{14}C content of a reservoir compared to the atmosphere (see Section 1.3.1.3; Anderson 1953; Aitken 1990).

1.3.1.2 Fluctuations of radiocarbon in the atmosphere

The natural fluctuations of ^{14}C are due to a non-constant generation of the radionuclide over time, partly due to variations in solar activity (Korf and Mendell 1980; Suess 1986). The flux of particles emanating from the sun, the 'solar wind', vary with time as does cosmic radiation reaching the atmosphere, and this is how the radionuclide is generated (Korf and Mendell 1980). These solar fluctuations are the origin of 'wiggles' visible in the calibration curve (see Section 1.3.2.2; Figure 1-9). The nuclides generated are deflected by the geomagnetic field of the earth thus an increase in the magnetic field results in the reduction of ^{14}C production (Aitken 1990). Even though most of the geographical variation in latitude disappears with the rapid mixing in the atmosphere, differences in atmospheric ^{14}C between Northern and Southern hemispheres are visible (Aitken 1990; Bowman 1990; McCormac *et al.* 2002; Hogg *et al.* 2013; Reimer *et al.* 2013).

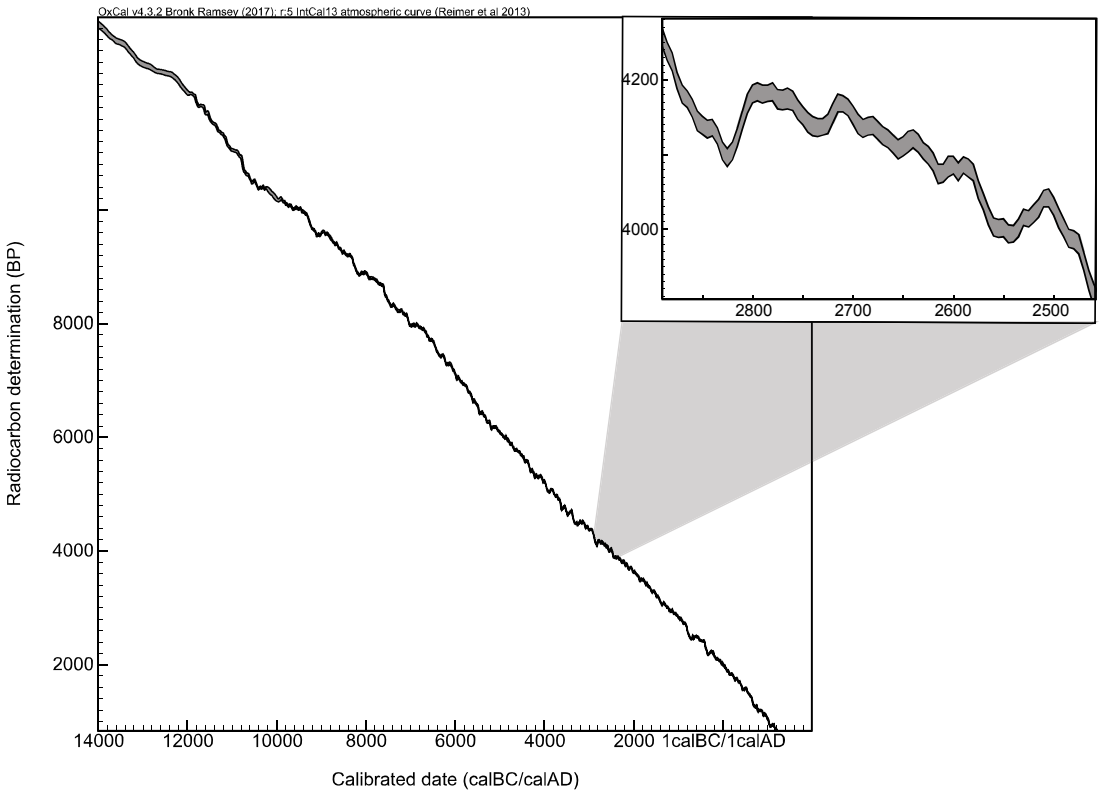

Figure 1-9: Northern hemisphere radiocarbon calibration curve IntCal13 (Reimer *et al.* 2013) extracted and adapted from OxCal v4.2 (Bronk Ramsey 2009). The curve plots radiocarbon determinations (BP) plotted against the calendar age (cal BC/AD) and shows the natural fluctuations of the ^{14}C atmospheric rate. The magnification shows the 'wiggles' in the period 3000 to 2500 cal BC.

Human activities have been proven to affect the amount of CO_2 in the atmosphere. The first human impact is the burning of fossil fuel at the end of 19th century (Suess effect; Suess 1955; Stuiver and Quay 1981) causing a depletion in ^{14}C in the atmosphere. The second change caused by human activity was due to the testing of nuclear weapons, starting in the early 1950's (Rafter and Fergusson 1957). This generated artificial ^{14}C, increasing dramatically the ^{14}C rate in the atmosphere. Testing lasted until 1963 when agreements about their cessation were signed, marking beginning of the return to natural atmospheric rates of ^{14}C production (Taylor 1987). This part of the calibration curve (Section 1.3.2.2) is known as the 'bomb peak' (Figure 1-10; Rafter and Fergusson 1957).

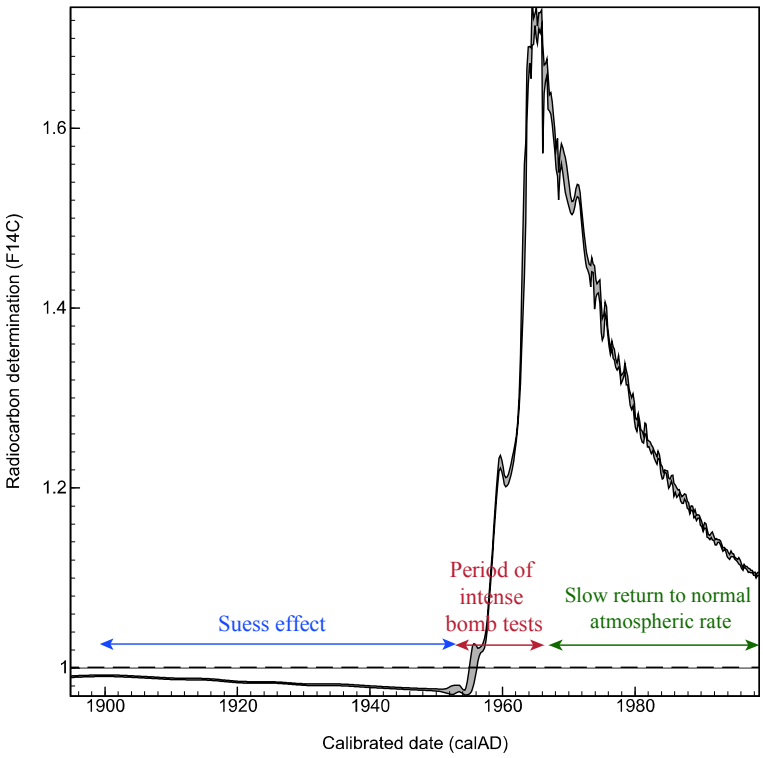

Figure 1-10: Radiocarbon determination plotted against calendar years from 1900 to present time, showing the Suess effect and bomb peak. Figure extracted and adapted from the calibration curve Bomb 13 NH3 in OxCal v4.2 (Bronk Ramsey 2009).

1.3.1.3 Fluctuations of radiocarbon in the biosphere

In the biosphere, different carbon pools, or reservoirs (e.g. atmosphere, oceans), have a radiocarbon content of different concentrations to the atmosphere due to different speed of the turnover rate of CO_2 (Aitken 1990; Lanting and van der Plicht 1998; Alves *et al.* 2018). The difference from atmospheric CO_2 is of particular importance for marine environments, freshwater or volcanoes, and it is known as the reservoir effect (Suess 1953; Deevey *et al.* 1954; Craig 1957; Muzzolini 1982). The organisms obtaining their carbon from such sources (e.g. marine or freshwater fish) will have an 'apparent ^{14}C age' usually older than the real one because the 'modern' level of radiocarbon has been diluted due to long residence times of the ^{14}C (e.g. marine environments) or mixed with infinite age carbon (e.g. volcanoes; Lanting and van der Plicht 1998).

Aquatic organisms are mainly affected by such reservoirs. The residence time of ^{14}C in the atmosphere is limited to a few decades against a thousand year in deep ocean, thus, the average marine reservoir effect for surface water is of ca. 400 years towards older values (Alves *et al.* 2018). Where water is present in volcanic areas, carbon dioxide from geological origin can be ejected from underground into the water and, similarly, for fresh water in limestone areas, infinite age carbonates can dissolve in water: this is known as the 'hard water effect' (Suess 1953; Deevey *et al.* 1954; Craig 1957).

1.3.2 Measurement of the radioisotope

1.3.2.1 Instruments to measure the radioisotope

Radiocarbon determinations can be performed in two ways, by: (i) measuring decay events, using liquid scintillation counting (LSC), or (ii) directly measuring the amount of ^{14}C in an organism, using accelerator mass spectrometer (AMS). The latter technique is now the most widely used, because of smaller sample sizes required and faster analysis time to reach a required level of precision (e.g. Synal *et al.* 2007; Fedi 2009).

An AMS is a special mass spectrometric method, which allows the separation of the radioisotope of carbon from the stable ones, and also its isobars (Bowman 1990). In practice, materials are introduced into an AMS as graphite or gaseous CO_2. The C samples are ionised in the ion source by a heavy beam of caesium ions (Cs^+). The negative carbon ions created are ejected from the ionisation chamber and go through a low energy magnet allowing the selection of molecular species with the masses 12, 13 and 14, which are transferred into the accelerator (Litherland 1987). At the entrance, the beam is accelerated into the terminal containing an electron stripper, allowing the generation of positive ions, which are repelled from the terminal and accelerated to ground potential at the end of the accelerator (Litherland 1987; Synal *et al.*

2007). The molecular species then enter a high energy magnet, which separates them based on their *m/z* ratio and allows the selection of ^{14}C isotope only for detection (Litherland 1987). The ^{12}C and ^{13}C ions, collected in faraday cup, is essential as it allows $^{14}C/^{12}C$ ratio measurements and correction from fractionation in the instrument (Synal *et al.* 2007).

Radiocarbon dating with an AMS uses graphite targets, requiring 1 mg of C but lately analysing micrograms of carbon (Santos *et al.* 2007; Shah and Pearson 2007) as graphite targets or by directly analysing the CO_2 with a gas ion source (Bronk Ramsey and Hedges 1987; Fahrni *et al.* 2013; Wacker *et al.* 2013a) was achieved with the new advances in AMS technologies. The latest generation of AMS, such as MICADAS (MIni radioCArbon DAting System; Figure 1-11; Synal *et al.* 2007) are more compact and allow to reduce the time of analyses. The MICADAS uses an acceleration potential that is reduced to 200 kV allowing to minimise the acceleration unit and thus instrument size. It achieves high sensitivity ^{14}C measurement at natural levels by the reduction of molecular interferences in the detector (Synal *et al.* 2000). With this instrument a new ion source was designed and allowed extraction energies of ions up to 40 keV reducing the time necessary to achieve a require level of precision in ^{14}C measurements (Synal *et al.* 2007).

Conventionally, unknown materials to be dated are analysed alongside standards to assure normalisation (using the NIST standard Ox II) and background corrections (using an infinite age standard; e.g. Wacker *et al.* 2010a; Dunbar *et al.* 2016). Other standards (e.g. IAEA, VIRI ; Rozanski *et al.* 1992; Scott *et al.* 2007b), of similar age range and material type to the unknown material dated, are also measured to validate the pre-treatment (Section 1.3.3.3) and corrections applied on the measurements.

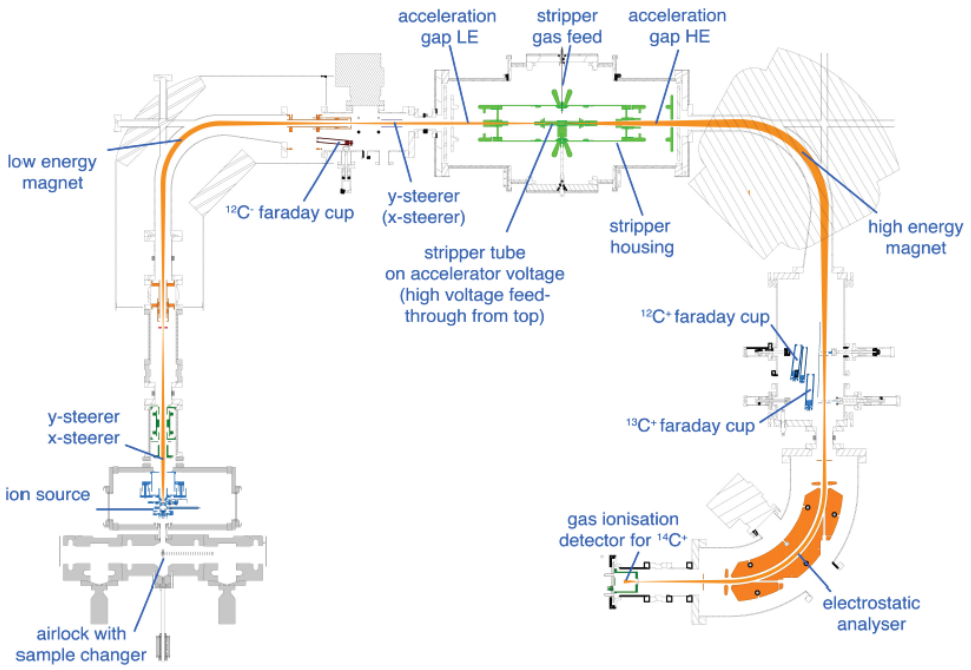

Figure 1-11: Schematic of a MICADAS AMS. From Ionplus (2015).

1.3.2.2 Calibration and statistical analysis

It should be noted that a radiocarbon determination using the half-life of the isotope does not provide a calendar age. This is due, as discussed above, to the creation in the stratosphere, of ^{14}C nuclides at a non-constant rate, therefore single events separable in time can exhibit the same radiocarbon ages (Bowman 1990). The $^{14}C/^{12}C$ ratios obtained by AMS analysis are proportional to the sample activity and are converted by data reduction computer software (e.g. BATS Wacker *et al.* 2010a) in fraction modern $F^{14}C$ (= normalised activity of sample /normalised activity of standard Ox I or II) for post-bomb materials, or in conventional radiocarbon age expressed in years BP (before present) for pre-bomb materials (Eriksson Stenström *et al.* 2011). The conventional radiocarbon age uses the following conventions: (i) the Libby half-life, (ii) the year 1950 is defined as "zero" on the radiocarbon scale, (iii) use of oxalic acid standard, (iv) correction of fractionation (Equation 1-3) and (v) requires conversion into a calendar age, BC (Before Christ) or AD (*Anno Domini* or after Christ). A calibration

curve is, therefore, needed to relate the radiocarbon content at a particular time to a calendar age (Clark 1975).

The calibration curves are built using dendrochronology for atmospheric C or from modelled ocean response to dendrochronological data for marine C (e.g. Stuiver *et al.* 1998a; Reimer *et al.* 2004, 2013). Dendrochronology is a precise dating technique using the annual growth of tree rings (oak trees in Europe; Baillie 1995). The ring patterns of the same tree species (e.g. oak) are comparable among trees; thus, it is possible to cross-date wood timber using the overlapping ages of two ring sequences (Figure 1-12; Baillie 1995). Using this, a master chronology going back to prehistory (13,900 cal BP; Reimer *et al.* 2013) can be built. This dating technique can be directly applied at archaeological sites if tree ring sequences are available (e.g. timber from buildings, wooden trackways). The recording of ^{14}C determinations on individual rings with known age, allows the ongoing process of construction of the atmospheric calibration curves for northern (IntCal 13; Reimer *et al.* 2013) and southern (SH 13; Hogg *et al.* 2013) hemispheres. Several laboratories working together generate and cross-check the ^{14}C measurements on tree rings to allow the generation of accurate curves.

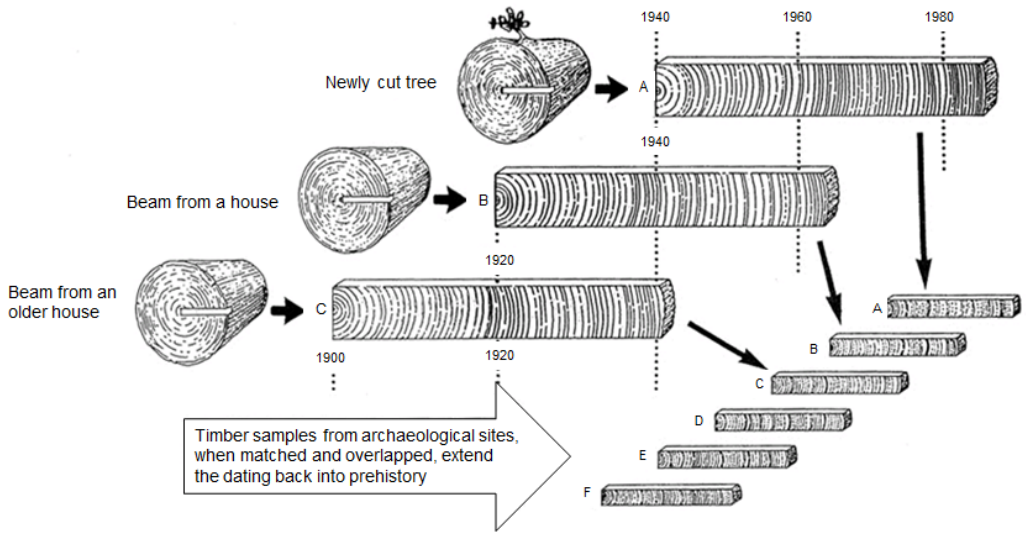

Figure 1-12: Tree-ring sequences of a modern tree and older ones (e.g. beam from a building). The rings overlapping, are counted and matched to build a chronology back to the prehistory. Adapted from Renfrew and Bahn (1991, Figure 4.15).

These curves can be directly integrated in calibration programs such as OxCal or Calib (Bronk Ramsey 2009; Stuiver *et al.* 2018). After calibration, the results are given as a posterior density probability for an event to occur at a particular time (Figure 1-13). Depending on the part of the curve the density probability can be spread over decades or even centuries (plateau effects).

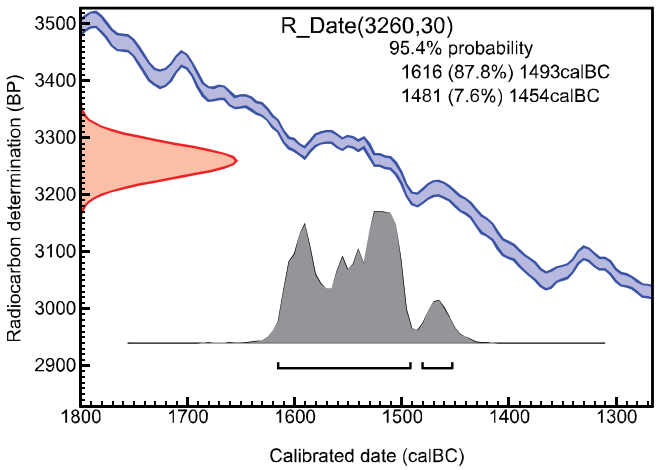

Figure 1-13: Northern atmosphere calibration curve for a calendar age ranging 200 to 2,000 cal BC showing a plateau between 700 to 400 BC. Example of a C sample measured at 3,260 ± 30 BP and its probability distribution to occur at a particular time after calibration in the OxCal program (v4.2 Bronk Ramsey 2009).

In order to reduce the uncertainty associated with calibrated ages, statistics, particularly the ones using Bayes theorem, have emerged as a tool to refine chronology to within a few years (Buck *et al.* 1991; Bronk Ramsey 1995, 2005, 2009; Bayliss *et al.* 2014). In simple chronological terms this theorem says that:

posterior distributions ∝ *prior* distributions * likelihood

where the *'prior* distributions' are information about relative age of the artefacts, the 'likelihood' the calibrated radiocarbon measurements on individual materials and the *'posterior* distributions' the calendar ages with reduced probability interval after modelling (Bronk Ramsey 2009). Such mathematical models use stratigraphy or seriation as *prior* information to relatively date the materials and estimate phase boundaries. The *prior* constrains

the ^{14}C measurements in a certain order, thus the probability distributions can be reduced. Numerous ^{14}C determinations of the successive phases to be dated are therefore required. This kind of analysis is becoming commonplace as it obtains precise estimates of the calendar age, such studies can be done site-by-site or at wider regional or country scales depending on the archaeological information required. For instance, Bayliss *et al.* (2015) focussed on dating the earliest contexts at the site of Çatalhöyük to estimate the beginning of the settlement and potential start of the use of pottery vessels in Europe, whereas Jakucs *et al.* (2016) focussed on dating the transition of Vinča culture to the formative and earliest group of the *Linearbandkeramik* culture.

1.3.3 Materials for radiocarbon dating

1.3.3.1 Selection of samples, taphonomy and reservoir effect

In practice, all living organisms containing carbon can be subjected to radiocarbon dating (Taylor 1987). However, their selection must be rigorous and performed in the light of the archaeological question and the nature of the material (Bowman 1990). Common organic materials to date for archaeological purposes are bones (collagen extraction), wood (cellulose), charcoal, shells (carbonates), antler, hair and charred residues (Taylor 1987). Aquatic organisms containing inorganic carbon, such as corals or shells, can also be used (Taylor 1987).

The taphonomy, the way organisms come to be preserved in an archaeological context (Martin 1999), can never been reconstructed with total confidence and can thus influence material selection for radiocarbon dating (Bowman 1990). The taphonomy study modifications that occurs after death such as degradation by erosion, weathering or microbial activities in the burial environment (Lyman 1994). The burial conditions influence material preservation, e.g. bones are better preserved in alkaline soils which would inhibit bone mineral dissolution (Child

1995) and alkanoic acids in pottery vessels are better preserved in acidic soils (van Bergen *et al.* 1998; Bull *et al.* 2000). The taphonomy also includes the post-burial history of a material such as exposure, transportation, breakage or re-burial (Martin 1999). Therefore, well-preserved materials that have not been moved after the first burial would be securely associated with their recovery context and would be appropriate candidates for ^{14}C dating. For instance, an articulated bone or refitted potsherd (several pieces of the same material) are less likely to correspond to an intrusive or residual material, in the context in which it is recovered, than a single piece of bone or potsherd which could have easily been transported. Some materials are a good source of carbon but not necessarily reliable in an archaeological context, especially if the material has been used or re-used after its "death" or are long lived materials. This is especially problematic in the case of wood or charcoal that survives well and might be used in more modern contexts. This is known as the "old wood effect" (Bowman 1990). Targeted materials for radiocarbon dating are, as a priority, ones that have a short life, have a rapid turnover into the burial environment, in addition to a good stratigraphic context, which avoids the selection of residual or intrusive materials.

Another factor to take into account prior to selecting organisms for dating is the reservoir effect on terrestrial organisms, which can also be affected by reservoir effect due to their diet or environment (Lanting and van der Plicht 1998). As mention previously (Section 1.1.2.3.1), C is incorporated in organism through the food chain and provide distinctive signatures based on their diet (Chisholm *et al.* 1982; O'Connell 1996; Schoeller 1999; Fernandes *et al.* 2014). The proportion of ^{14}C is affected across trophic levels similarly to $\delta^{13}C$ values. Marine organisms usually present a depletion in ^{14}C which would cause a depleted signal as well in the organisms feeding from them, and thus an older apparent age (Lanting and van der Plicht 1998). As an example, a study performed on human collagen with a known death date exhibited older radiocarbon dates (Lanting and van der Plicht 1998). These results suggested that the

individuals fed from mixed reservoirs including a source with a reservoir effect (probably by eating fish). Another study performed by Beavan-Athfield *et al.* (2001) showed an apparent age for a rat living in proximity of the Lake Taupo (New Zealand) to be over 2,000 BP with the aquatic plants in the lake dating from 4,500 to 500 years BP. This is because the lake and surrounding vegetation took up radiocarbon dead CO_2 due to close volcanic activity. Knowledge of the environment in which an organism lived, as well as its diet, is therefore of particular importance for reliable ^{14}C determinations. Traditionally, bulk isotope values of $\delta^{13}C$ and $\delta^{15}N$ are recorded at the same time as ^{14}C dating of collagen extracted from bones. Enriched $\delta^{15}N$ values in a trophic level are often indicative of a diet with a high marine component (Figure 1-4; O'Connell 1996). This is carried out as a check, to detect protein-rich diets (fish-eating) that might suggest a reservoir effect, which would bias the dates.

1.3.3.2 Contamination issues

Contamination potentially associated with the material to be dated is one of the most discussed phenomena in radiocarbon dating (Bliss 1952). Contamination can come from three major sources: (i) modern contamination, e.g. fingers, consolidant material, (ii) fossil contamination, e.g. solvent derived from petroleum or limestone of geological origin or (iii) intermediate ages contamination coming from the environment, such as carbonates precipitations or humic acids (Hedges and van Klinken 1992; Alon *et al.* 2002; D'Elia *et al.* 2007). The introduction of contamination modifies the activity in the following way (Equation 1-4 deriving from Aitken 1990,):

$$A_m = \%Cont * A_{cont} + (100 - \%Cont)A_s$$

Equation 1-4

Where A_m = activity measured (SI)
A_{cont} = activity of the contamination (SI)
A_s = activity of the sample (SI)
%Cont = fraction of carbon contamination introduced in the sample (%)

In the case of contamination with dead-carbon, i.e. A_{cont}= 0, the ^{14}C dates are biased with a value dependent only on the percentage of contaminant introduced (Figure 1-14a; Aitken 1990; Hedges and van Klinken 1992). For instance, 0.1 % contamination by dead radiocarbon presents an 8-year offset to older ages and 10 % contamination presents an 850-year offset to older ages.

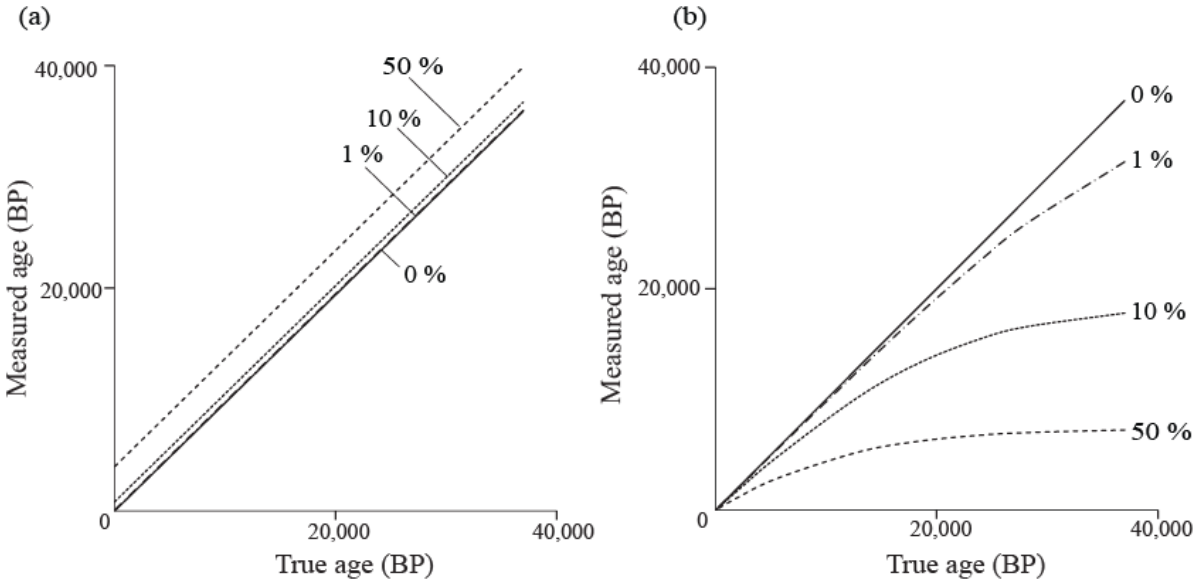

Figure 1-14: Measured age plotted against the true age for (a) contamination with fossil C (A_{cont} = 0) and (b) contamination with modern C (A_{cont} = 1). The lines correspond to contamination with exogenous C from 0 to 50 %. Adapted from Bowman (1990).

Contamination with modern carbon is more critical because it depends both on the percentage of contamination and the fraction modern of the contaminant (Figure 1-14b). Such contamination giving younger ages is of particular importance for really old organisms because, the older the organism, the bigger the effect of contamination is (Aitken 1990). For instance, 1% contamination with modern carbon causes a 30-year offset to a 2,500-year-old organisms whereas it causes a 4,000-year offset to a 34,000-year-old organism (Bowman 1990). This emphasises the importance of pre-treatment (see Section 1.3.3.3) to remove contaminants prior to dating archaeological samples.

One common source of contamination with old carbon comes from conservation treatments (i.e. glues, resins, varnish), which can add fossil carbon to artefacts (Rasmussen *et al.* 2001; Brock *et al.* 2018). Such contamination, therefore requires removal prior to dating, but the efficiency of pre-treatment is not always optimal, and it is advisable not to date such materials (Dee *et al.* 2011; Brock *et al.* 2018). Other common sources of contamination from the burial environment involves, for instance, the uptake of more modern C and the creation of carbonates on the material surface (Hassan *et al.* 1977; Stafford *et al.* 1987), or the adsorption of other molecular species from rootlet or groundwater such as humic acids (Hedges and van Klinken 1992; D'Elia *et al.* 2007).

1.3.3.3 Sample pre-treatments

Pre-treatment prior to radiocarbon dating is required to remove exogenous carbon associated with the material to be dated (Taylor 1987). Every material will be treated differently based on their nature and contaminants associated and the laboratory involved in the pre-treatment. The most common pre-treatments for archaeological materials with organic carbon involves an "Acid-Base-Acid" (ABA, Brock *et al.* 2010) wash that is adapted to the nature of the material, i.e. concentration of the acid/base, duration or temperature (e.g. Brock *et al.* 2010; Staff *et al.* 2014; Dunbar *et al.* 2016). The first acid wash is usually used to remove the carbonates created in the burial environment or dissolution of mineral matrices (e.g. bones), the base is used to remove the so-called "humic acids", and the second acid treatment eliminates modern CO_2 dissolved in the solution during the chemical processing (Brock *et al.* 2010). Such ABA pre-treatments can result in a considerable loss of material. Therefore, larger carbon sizes ca. 600 mg of bone for collagen preparation, ca. 20 mg for seeds or charred residues are needed to obtain at least 1 mg of carbon. Further work can also done depending on the material to be dated e.g. bleaching for plant remains (Brock *et al.* 2010).

In the case of archaeological bone most laboratories employ instead of an ABA pre-treatment a modified Longin method that involves an acid extraction of collagen and gelatinisation (Longin 1971) and can be followed by ultrafiltration (Bronk Ramsey *et al.* 2004b). Cremated bones (or tooth enamel) are however bleached before being treated with acetic acid (Brock *et al.* 2010; Dunbar *et al.* 2016). In the case of fragile and really precious materials, such as parchment or mummified tissues, the residues can be simply solvent or acid washed instead of ABA washes (Brock *et al.* 2010).

For archaeological materials with inorganic carbon (shells), an acid treatment is performed to etch the surface and remove any exogenous carbonate from recrystallisation, prior to treatment with phosphoric acid to convert the carbonates to CO_2 (Taylor 1987; Brock *et al.* 2010; Russell *et al.* 2011). Approximately 12 mg of carbonate is needed to generate 1 mg of graphite C.

1.3.4 Compound-specific radiocarbon analysis (CSRA)

1.3.4.1 Principles and instruments for CSRA

The idea of isolating single compounds for ^{14}C measurements rose in the late 1980's for the purification of amino acids in bone collagen and polycyclic aromatic hydrocarbons in the atmosphere (Stafford *et al.* 1987; Currie *et al.* 1989). The inception of routine CSRA was performed by Eglinton *et al.* (1996), whose aim was to achieve isolation of single fractions in ocean sediments for ^{14}C dating.

Sometimes, bulk dating materials and conventional pre-treatments do not allow the removal of all contaminants (e.g. bone collagen; van Klinken *et al.* 1994), thus isolation of single compounds to radiocarbon date materials at the molecular level can be considered to obtain a more accurate date, i.e. compound-specific radiocarbon analysis (CSRA; Eglinton and Pearson

2001). This kind of analysis allows the exclusion of exogenous contaminants and therefore potentially gives more reliable results. Also, in heterogenous matrices such as sediments and soils, a bulk date would introduce lot of variability and uncertainty on the ^{14}C determination due to the complex mixtures of diverse sources of C (Eglinton and Pearson 2001) whereas a date at the molecular level would allow to relate it to a known source (Eglinton *et al.* 1996).

The development of compound-specific analyses using the preparative capillary gas chromatography (PCGC) or (ii) the preparative high-performance liquid chromatography (Preparative HPLC) is of particular importance as it allows the dating of materials that could not be dated by traditional methods and overcomes limitations arising due to contamination. CSRA was nonetheless a technical challenge (Eglinton *et al.* 1996) as all sources of contamination associated with the procedure (which could vary with the nature of molecules isolated and instrument used) required quantification and elimination allowing the obtention of purified compounds.

The first attempt to use preparative capillary gas chromatography (PCGC) for the isolation of compounds for radiocarbon analysis was performed by Eglinton *et al.* (1996) using reference alkanes, FAs and sterols of infinite (petroleum wax), modern (living plants) and intermediate (oil for an Egyptian vessel dated from 1498 BC) ages. The study was promising and the first of many which focussed on the PCGC isolation of other molecules analysable by GC: (i) *n*-alkanes from sediments (Eglinton *et al.* 1997), (ii) polycyclic aromatic hydrocarbons from atmospheric aerosols (Currie *et al.* 1997), (iii) phenolic compounds from lignin (McNichol *et al.* 2000), (iv) fatty acids from oceanic sediments (Ohkouchi and Eglinton 2008) or (v) fatty acids from archaeological pottery vessel (Stott *et al.* 2001). This technique is most widely used for the analysis of compounds from sediments and natural matrices.

PCGC consists of a regular GC (gas chromatography) with FID (flame ionisation detector) and autosampler coupled to a preparative device (Figure 1-15; Rijks and Rijks 1990). The preparative system consists of an effluent splitter connected to a series of collection traps (usually 7). Another effluent splitter sends ~1 % of the material to the detector, and ~ 99 % through a heated transfer line, bringing the analyte from the end of the GC column to the trapping system (Eglinton *et al.* 1996). Eglinton *et al.* (1996) recognised typical sources of contaminations to come from (i) degradation of column stationary phase, (ii) incomplete removal of solvent after purification and (iii) extraneous C added for derivatization of certain molecules for chromatographic isolation. Later Ziolkowski and Druffel (2009) recognised memory effect to be another source of C. These requires quantification and suppression to obtain the accuracy needed with CSRA.

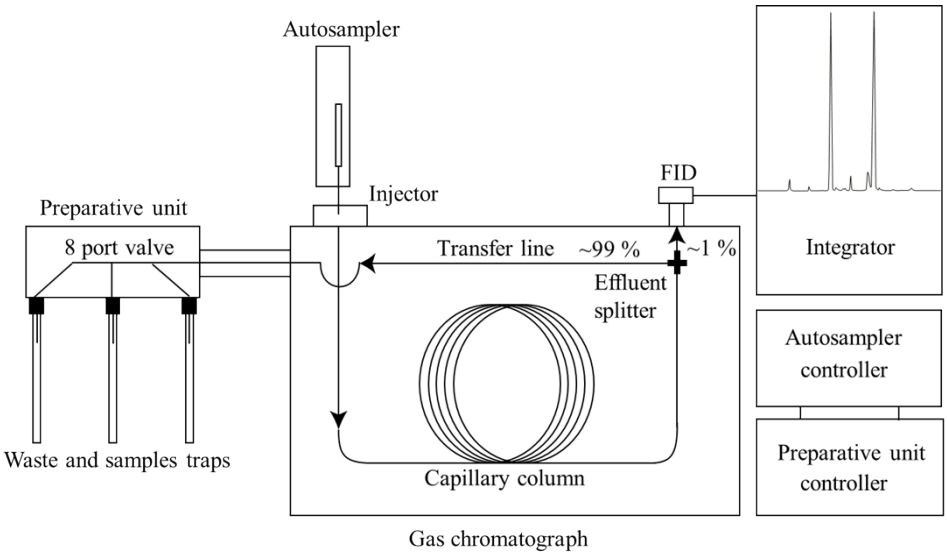

Figure 1-15: Schematic of a preparative capillary gas chromatography instrument.

The second instrument used for CSRA is the preparative HPLC. This instrument is of particular use for polar, non-volatile and thermally unstable analytes difficult to isolate by PCGC (Eglinton and Pearson 2001). This technique is mostly used in reversed-phase mode for amino acids and carbohydrates isolation. Preparative HPLC has been useful for the separation of

amino acids or peptides from bone collagen since the early 1990's (van Klinken 1989; van Klinken and Mook 1990; van Klinken and Hedges 1992; van Klinken et al. 1994; McCullagh et al. 2010; Marom et al. 2013; Deviese et al. 2018). Such an approach is complementary to bulk collagen analysis in cases where collagen is poorly preserved and where ultrafiltration pre-treatments are limited due to remaining contamination issues (Brock et al. 2010; Marom et al. 2013). HPLC has also been also used for isolation of alkenones from sediments, and offered a faster alternative to PCGC (Ohkouchi et al. 2005).

The preparative HPLC differs from the analytical variant, focusing isolation and purification of products as opposed to qualitative/quantitative profiles (Eglinton and Pearson 2001). In practice, rather than sending the eluent to the waste, it is diverted to individual tubes based on the retention times of compounds of interest. In contrast to PCGC this instrument also allows the injection of more concentrated lipid extracts and reduces the isolation time of the components (Eglinton and Pearson 2001). Contamination with residual solvent can be overcome using an aqueous mobile phase. However, the degradation of column stationary phase in HPLC instrument is more critical than with PCGC and the instrument is also subjected to memory effect (Eglinton and Pearson 2001).

1.3.4.2 Towards CSRA of lipid residues extracted from pottery vessels

It is not uncommon for archaeological sites to demonstrate a dearth of organic materials resulting in difficulties in dating (e.g. no bone survival in acidic soils; Child 1995), however, such sites often contain abundant pottery assemblages. The absorbed organic residues associated with such pots offer a valuable means of dating such sites, as temper and visible residue dating are limited (Section 1.2.3). Furthermore, dating such residues would allow pottery seriations to be directly refined to calendar ages, overcoming taphonomic uncertainties

associated with dating associated materials co-deposited in the same contexts. The timing of inception of new commodities (e.g. milk, maize, millet etc), is an important question in archaeology and first clues of their use, are often recovered, from pottery vessels (Section 1.1.2). Thus, directly and reliably dating pottery vessels would open the way to refining relative chronologies made from seriation, dating the inceptions of new commodities directly by their residues in potsherds and dating sites, that could have been not be dated previously by other materials.

Intensive analyses of pottery vessels from different locations performed by Evershed and co-workers over the years (e.g. Evershed *et al.* 1990, 2008b; Dudd and Evershed 1998; Copley *et al.* 2003; Hansel *et al.* 2004; Reber and Evershed 2004; Dunne *et al.* 2012; Correa-Ascencio *et al.* 2014; Cramp *et al.* 2014a, 2014b; Roffet-Salque *et al.* 2015) have demonstrated that lipid residues are often preserved in high concentrations within the vessel wall and are commonplace in the archaeological record (Evershed *et al.* 2002a). Also, with all the knowledge obtained from the chromatographic and isotopic analysis of lipid deposition, composition, degradation, contamination and means of assessing potential reservoir effects (Section 1.1.2), this class of carbonaceous residue offers major advantages for the identification of the best candidates for ^{14}C determinations. Adsorbed lipids are widely untapped for ^{14}C analyses but offer more certainty on the source of C (e.g. lipids from terrestrial animals) compared to surface residues which are not always analysed before being radiocarbon dated (Teetaert *et al.* 2017). In addition, the lipids: (i) have a fast turnover in the organism from which they derive then are not exchanging C with the exterior, (ii) are protected within the vessel wall from exogenous contaminants (i.e. no carbonate or humic acid contamination), (iii) can be recovered in concentration above 1 $mg.g^{-1}$ of clay (allowing sufficient C to be extracted for a radiocarbon measurement), and are therefore good candidates for ^{14}C determinations (Stott *et al.* 2001). Degraded animal fats are the residues which present the highest lipid concentrations, thus these

represent the best candidates for a ^{14}C determination at the molecular level compared to plant/beeswax or other residues found in potsherds. These later rarely present lipid concentration above 500 $\mu g.g^{-1}$, thus they would not be routine samples for CSRA due to the lower C fraction available.

Having recognised how important it would be to directly and accurately date pottery using CSRA on animal fats, attempts made by Stott *et al.* (2001) yielded promising preliminary results. As opposed to previous studies where bulk dating of lipids (e.g. Hedges *et al.* 1992) was carried out, PCGC was used for CSRA dating. The approach adopted allowed the elimination of potential contaminants from storage and handling as well as the residual solvent used for the extraction. Therefore, only compounds which have an archaeological origin are dated instead of a mixture of all the compounds present in the TLEs. However, overall the pots dated by Stott *et al.* (2001), showed significant variability between the two fatty acids (FAs) measured. The origin of such variability which was inconsistent between potsherds and thus unclear, but it indicated that further work was required to determine its origin and, thus, improve the accuracy of the method. The work on the Sweet Track by Berstan *et al.* (2008), started with lipid residue analysis to detect the sherds with suitable concentrations and lipid for dating and to detect contaminants likely to affect radiocarbon dates. The lipids dated showed a better agreement between the FAs dates, however, the dates obtained were younger by ca. 200 years than the dendrochronological date of the construction of the track way suggesting some methodological problems remained.

The CSRA approach using PCGC having showed to be useful in various applications (e.g. Eglinton *et al.* 1996). For archaeological potsherds, these failed the accuracy despite potsherds being selected carefully from precisely dated sites and contexts. Therefore it suggests that all the contamination issues present in the procedure employed by Stott *et al.* (2001) and Berstan

et al. (2008) were not resolved (e.g. cross-contamination, Ziolkowski and Druffel 2009). The methodological issues raised by these studies recognised that new approaches would need to be developed to refine the CSRA method. Such developments require the use of standards materials and a careful selection of pottery from well-dated sites to enable accuracy and reproducibility of the method to be rigorously assessed before considering its wide application to sites of unknown age.

1.4 Aims and objectives

Being able to reliably radiocarbon date pottery vessels in an accurate and reproducible way has been a goal for many years. If such materials could be dated routinely it would open up the range of datable archaeological sites that cannot be dated from other materials. The research presented in this thesis is built on the hypothesis that CSRA dating of lipids is the solution to dating archaeological pottery, offering the potential to achieve optimal accuracy and precision, and that the exogenous carbon that foiled previous attempt can be identified and eliminated (Stott *et al.* 2001, 2003; Berstan *et al.* 2008).

The aim of this thesis is to achieve the accuracy required to routinely date by a CSRA approach pottery vessels based on analysis of absorbed lipid residues. The first aim is to identify and suppress all the sources of contamination associated with the overall procedure. Then the method requires application on a corpus of known age pottery vessels to evaluate the accuracy of the method prior to demonstrating its usefulness to answer archaeological questions. The specific aims of this thesis are:

(i) Improve the CSRA method by identifying, quantifying and eliminating all sources of contamination associated with the isolation procedure in the PCGC to successfully

isolate single fatty acids without any contaminants biasing their ^{14}C age. This will focus on contamination from the instrument, the purity of single compounds after isolation, and cross-contamination between trapping sequences (Chapter 3).

(ii) Apply the method to a range of archaeological materials from archaeological sites of known age to test the reliability and accuracy of the CSRA method. This will be carried out on a range of pottery from sites of significantly different ages, well-dated by different materials and with different burial environments (Chapter 4).

(iii) Analyse pottery vessels from one well-dated region (Alsace, France), undertake lipid residue analysis as a prelude to generating CRSA dates from a sub-set of lipid residues, for comparison with available dates on other materials. This will be used to demonstrate the importance of performing rigorous lipid residue analysis prior to ^{14}C dating sherds (Chapter 5).

(iv) Apply the CSRA method and demonstrate its use as a tool for quality control and answering archaeological questions, focussing on the direct dating of the early dairying in central Europe (Chapter 6).

(v) Study of lipid residues from a coastal site, with known aquatic exploitation, will demonstrate how reservoir effects and mixed diets will affect CSRA but how molecular and carbon isotope proxy data on the lipids can be used to correct for the marine reservoir effect (Chapter 7).

Overall, the results presented in this thesis will demonstrate the realisation of CSRA of lipids from pottery as a viable new dating tool in archaeology.

Chapter 2.

Materials and methods

Chapter 2. Materials and methods

2.1 Introduction

This chapter presents reference and archaeological materials studied for the development of new CSRA method of archaeological lipids and the methodology employed (i.e. analytical protocols, instrumentation and data processing). The protocols used came either from published literature and are referenced as such or, have been established in the context of this thesis and are referred to the relevant chapters.

2.2 Materials

2.2.1 Reference materials

All reference materials used this thesis with their purity and provenance are summarised in Table 2-1.

Table 2-1: Summary of reference materials used in this thesis.

Name	Material type and purity	Supplier/ reference	Use in the thesis	Section
Palmitic acid **Stearic acid**	FA (>98%) FA (>98%)	Sigma Aldrich (Poole, UK)	Age correction of FAME methyl group	3.3.3
Methyl palmitate **Methyl stearate**	FAME (>98%) FAME (>98%)	Sigma Aldrich	Assessment of exogenous C during PCGC isolation. Standard for NMR	3.4; 3.5
Hexamethylcyclotrisiloxane **Octamethyltetracyclosiloxane** **Decamethylpentacyclosiloxane**	PDMS (>98%) PDMS (>98%) PDMS (>98%)	Sigma Aldrich	Standard of 'bleed products' for NMR and GC-Q/TOF analyses. Calibration of NMR instrument	3.4; 3.5
Ox II	Oxalic acid	NIST (Maryland, USA)	Standard for normalisation in ^{14}C dating	3; 4; 5; 6; 7
Phthalic anhydride	Phthalic anhydride	Sigma Aldrich	Blank standard for background correction in FAs/pot dating	3; 4; 5; 6; 7
IAEA C7 **IAEA C8**	Oxalic acid Oxalic acid	IAEA (Vienna, Austria)	Standard reference in FAs/pot dating	3; 4; 5; 6; 7
TIRI F **TIRI K**	Doublespar Carbonate	Gulliksen and Scott 1995	Blank standard for background correction in shells dating Standard shells dating	7
VIRI F **Yarton**	Horse bone Bovinae femur	Scott *et al.* 2010b Cook *et al.* 2012	Standard collagen dating Blank standard for background correction in collagen dating	7
VIRI P	Charcoal	Scott *et al.* 2010a	Standard seed/surface residue dating	4.4.2.4; 7

HPLC grade solvents were purchased from Rathburn Chemical Ltd (Walkerburn, UK) and deuterated chloroform used as solvent for NMR analyses ("100 %", 99.96 atom % D) from Sigma Aldrich (Poole, UK).

2.2.2 Archaeological bog butters

Bog butters (large quantities of fats) were selected as ideal archaeological samples to demonstrate the effectiveness of the CSRA method established in this thesis because of their size and hydrophobic nature (see Section 4.3). Sub-samples were provided from six archaeological bog butter by the National Museum of Ireland (Dublin, Ireland). These were previously chemically analysed in the context of R. Berstan PhD thesis (Berstan 2002).

2.2.3 Archaeological pottery vessels

The archaeological sites (described in the following chapters) were chosen carefully by being previously dated or presenting archaeological questions to answer with radiocarbon measurements. All potsherds for ^{14}C dating were selected based on their lipid profiles (presence of animal fats), their lipid concentrations (> 500 $\mu.g^{-1}$) and their size (typically > 20 g). The full list of archaeological pottery vessels, contexts associated, and ORA results are given in the Appendices.

2.2.3.1 UK potsherds

Two pottery vessels were provided from the Sweet Track (Somerset Levels, UK) by S. Minnitt (The Museum of Somerset, Taunton, UK). These pots were ORA analysed by and previously ^{14}C dated by Berstan *et al.* (2008; Chapter 4, Appendix 2). This site is dated precisely by dendrochronology (Hillam *et al.* 1990) and present wetland burial conditions.

A total of 30 potsherds were supplied from the site of Cliffs End Farm (Isle of Thanet, Kent, UK) by A. Barclay (Historic England, UK). These were chosen as reference materials by being previously ^{14}C dated from their surface residues (McKinley *et al.* 2014). The potsherds were ORA analysed as part of this thesis, and four were ^{14}C dated (Chapter 4, Appendix 5).

A total of 131 potsherds from the site of Bornais (South Uist, Outer Hebrides, UK) were ORA analysed previously by L. Cramp (forthcoming), 14 of which were ^{14}C dated in this thesis. An additional 49 potsherds were provided from the site by N. Sharples and K. Harding (Cardiff University, Cardiff, UK) for ORA and ^{14}C dating (Chapter 7). These potsherds were selected to investigate the influence of marine products processing for radiocarbon dating. Additionally, 10 terrestrial animal bones, 15 shells and 11 fish bones from the same contexts of the potsherds were sampled for ^{14}C dating to complete the reference ^{14}C measurements at the site (Marshall *et al.* 2016; Marshall *et al.* forthcoming; Chapter 7, Appendix 8).

2.2.3.2 African potsherds

Two potsherds and well-preserved *Sorghum* seeds were provided from the site of Takarkori Rockshelter (Acacus Mountains, Libya) by S. di Lernia (University of Rome, Italy). These potsherds were previously ORA analysed (Dunne *et al.* 2012) and bulk radiocarbon dated (unpublished data of J. Dunne; Chapter 4, Appendix 3). The different phases of the site and *Sorghum* seeds were previously radiocarbon dated (Biagetti and di Lernia 2013; Mercuri *et al.* 2018). This site presents an arid burial environment.

Three pottery vessels were provided from Samburu Pastoralist (Kenya) by J. Dunne (University of Bristol, UK) and M. Grillo (University of Wisconsin, UK). These were previously ORA analysed by Dunne *et al.* (2018). To unravel the debate on their age three potsherds were CSRA dated (Dunne *et al.* 2018; Chapter 6, Appendix 7).

2.2.3.3 Turkish potsherds

A total of 15 potsherds were provided from the site of Çatalhöyük East (Turkey) by A. Marciniak (Poznan University, Poland). These were previously ORA analysed by Roffet-Salque and Evershed (In press). The potsherds come from a site presenting a precise stratigraphy which was precisely radiocarbon dated and modelled using Bayesian statistics (Marciniak *et al.* 2015; Chapter 4, Appendix 4).

2.2.3.4 Central European potsherds

A total of 871 pottery vessels from the Alsace region (France) were first sampled for ORA, following, when possible, guidelines by Charters *et al.* (1993b), i.e. sampling the upper part of the vessel which contains the highest lipid concentrations, with an even representation of both decorated and undecorated vessels (Chapter 5, Appendix 6). Potsherds were provided from the sites of Bischoffsheim and Rosheim by B. Schnitzler (Palais Rohan, Strasbourg, France), D. Mini, P. Lefranc (Inrap, Strasbourg, France) and A. Denaire (Antea Archéologie, Habsheim, France), from the site of Colmar by S. Plouin (Musée Unterlinden, Colmar, France), from Sierentz by L. Pinéro (Musée Historique de Mulhouse, Mulhouse, France) and from Ensisheim by A. Mulot (PAIR, Selestat, France). The sites of Bischoffsheim and Rosheim were included previously in a regional dating program based on the regional seriation of Neolithic pottery (Denaire *et al.* 2017). A total of 26 potsherds from these sites were CSRA dated.

A total of 24 pottery vessels from the *Linearbandkeramik* culture sites across central Europe (France, the Netherlands, Germany, Poland and Hungary) were ORA analysed at the University of Bristol as part of the NeoMilk project funded by the European Research Council (FP7-IDEAS-ERC/324202). The potsherds were selected to date directly early dairying in central Europe (detailed selection in Chapter 6 and Appendix 7).

2.3 Analytical protocols

2.3.1 Cleaning procedures

2.3.1.1 Laboratory equipment

Prior to use, to remove contaminants, the glassware was cleaned with Decon 90 and laboratory grade acetone and pre-combusted (450 ^{o}C > 2 h). Volumetric glassware and equipment with thick glass (i.e. mortar and pestle) were not furnaced but washed with HPLC grade DCM (or MQ-water) and dried in a drying oven. Before and after use syringes were cleaned with HPLC grade ethyl acetate and DCM. Before use tweezers and spatula were cleaned with HPLC grade DCM or ethanol then blow dry.

2.3.1.2 Mechanical cleaning and sampling of archaeological samples

Pottery vessels, animal bones and shells were photographed in a lightbox before sampling for records of the shape. To remove surface contaminants, a small part of the potsherd (~ 2 - 7 g) was cleaned with a modelling drill then sampled using hammer and chisel and ground to fine powder using mortar and pestle. The surface of the bones (ca. 500 mg) and shells (ca. 30 mg) was cleaned after sampling with a cutting drill then coarsely grounded using mortar and pestle.

2.3.2 Protocols for lipid residue analysis of pottery vessels

2.3.2.1 Methanolic/sulphuric acid extraction

For ORA (Correa-Ascencio and Evershed 2014), approximately 1 to 2 g of ground potsherd were weighed into a clean culture tube (I) with stopper and 20 µL of internal standard (IS; *n*-tetratriacontane) at 1 mg.ml^{-1} was added. The lipids were extracted using a solution of

H_2SO_4/MeOH (4% *v/v*, 5 mL, 70 ºC, 1 h,). The supernatant of culture tube I was then centrifuged (2500 rpm, 10 min) and transferred to a clean culture tube (II) before adding double distilled water (2 mL). *N*-hexane was added (2 x 3 mL) to culture tube I and the supernatant transferred to culture tube II. Following this, 2 x 2 ml *n*-hexane was added directly to the H_2SO_4/MeOH solution in culture tube II and whirlimixed to extract the remaining residues, then transferred to the 3.5 mL vials and blown down until a full vial of *n*-hexane remained. A procedural blank (same protocol without grounded clay in culture tube) was prepared and analysed alongside every batch of archaeological materials to assess whether contamination was introduced during the protocol. Before analysis, an aliquot of the total lipid extract (TLE; 1/4) was derivatised by the addition of BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide; 20 µL, 70 ºC, 1 h). Excess BSTFA was blown down at 40 ºC under a gentle stream of nitrogen, and an appropriate amount of *n*-hexane was added, prior to analysis with GC, GC-MS and GC-C-IRMS (Sections 2.4.1, 2.4.2, 2.4.3).

2.3.2.2 Chloroform/methanol extraction

For ORA at high temperature (Evershed *et al.* 1990), approximately 1 to 2 g of ground sherd was weighed into a 28 mL vial and 20 µL of the IS at 1 $mg.mL^{-1}$, was added. The lipids were extracted by sonication (2 x 10 mL x 20 min), with a solution of chloroform/methanol (2:1 *v/v*). After decanting, the solution was centrifuged (2500 rpm, 10 min) then the supernatant transferred into a 3.5 mL vial and the solvent blown down under a gentle nitrogen stream (Evershed *et al.* 1990). A procedural blank (Section 2.3.2.1) was performed with every batch of extractions to assess contamination during the protocol. An aliquot of the TLE (1/4) was eluted through a silica gel column to remove any particulates. The solution was dried under a stream of nitrogen before derivatization with BSTFA (40 µL, 70 ºC, 1h). Excess BSTFA was

blown down at 40 ºC under a gentle nitrogen stream before the addition of an appropriate amount of *n*-hexane for analysis with HTGC and HTGC-MS (Sections 2.4.1, 2.4.2).

2.3.3 Protocols for quantification of exogenous C

2.3.3.1 Preparation of a FAME standard solution

The $F^{14}C$ values of $C_{16:0}$ and $C_{18:0}$ FAMEs standards (Section 2.2.1), were directly measured by AMS (Section 2.4.9). The weighted average of the five replicates serves as a reference value. From these standards, a FAME standard solution was prepared in hexane, containing each FAME at a concentration equivalent to 5 μgC·μL−1, which is the target concentration for FAMEs extracted for the PCGC isolation of archaeological samples in order to obtain ca. 200 μg of C (see Section 3.3.1).

2.3.3.2 Preparation of single compounds for NMR analysis

NMR analyses were performed to asses background C contamination from PCGC instrument (Chapter 3). Individual compounds isolated by PCGC into individual Gerstel traps (G-trap; denoted $TC_{16:0}$ and $TC_{18:0}$) were submitted to NMR (Section 2.4.4). The compounds were recovered from the traps using 1 mL of DCM or *n*-hexane, blown down to dryness and dissolved into 200 μL of $CDCl_3$ (100%). Then 50 μL was aliquoted and transferred to a 1.7 mm NMR tubes using a gas-tight syringe for NMR analysis. Another 50 μL was aliquoted to a 3.5 mL vial, 50 μg of an internal standard (*n*-tetratriacontane) added before blowing down to dryness, dissolving in 500 μL of *n*-hexane and quantifying the amount of compound isolated by GC (Section 2.4.1).

The compounds, isolated in the solventless trap (S-trap, Chapter 3), were recovered by pushing the glass wool into a test tube with a furnaced Pasteur pipette. The trapped compounds were

extracted from the wool using 2 x 100 µL of $CDCl_3$ (100%), then 50 µL were aliquoted and quantified using the same protocol as described above.

For each batch, 2 blanks (pure solvent added in an NMR tube before the recovery and transfer of the compounds and after the transfer of the last analyte) were run at the same time to evaluate both possible contaminants in the solvent and cross-contamination in the syringe used to transfer the compounds.

Stock solutions containing known concentrations of $C_{18:0}$ FAME and hexamethylcyclotrisiloxane were prepared volumetrically to produce an NMR calibration curve for quantification by NMR. These solutions contained the FAME at 1 $mg \cdot mL^{-1}$ and siloxane in varying concentrations, from 1 to 1.10^{-6} $mg \cdot mL^{-1}$, diluted in chloroform-d solvent.

2.3.3.3 Protocol for the evaluation of the efficiency of the trap designs

The efficiency of both trap designs introduced later in Chapter 3 was evaluated with the same compounds processed for the NMR study. The amount of modern FAMEs trapped was evaluated with a second aliquot and quantified with GC against an internal standard (Section 2.4.1). The waste trap (T_W) was also analysed to verify the amount of FAMEs lost in the waste trap. As opposed to the traps $TC_{16:0}$ and $TC_{18:0,}$ the contents of T_W were dissolved into 50 µL of *n*-hexane and quantified against 5 µg of IS.

For the new S-trap design (see Section 3.5), glass wool (Assistent, Sondheim, Germany) was fitted into the tubes with clean Pasteur pipette and pre-combusted before analysis. For the S-traps, the potential loss of compound condensed on the trap wall after pushing out the glass wool was evaluated by washing the traps with 500 µL of *n*-hexane. Washings were collected

into a 3.5 mL vial, blown down, and then prepared for GC analysis (Section 2.4.1) as described above for the contents of T_W.

2.3.4 Protocols for radiocarbon determinations

2.3.4.1 Pre-treatments of bog butters for radiocarbon determinations

Bog butters (see Section 4.3) were sampled from the centre of the mass and could therefore be regarded as being free from external contamination (because they were isolated from the burial environment). For this reason, the fats were directly bulk dated without pre-treatment. The bog butters (ca. 20 mg) were prepared for CSRA by following the protocol presented in Section 2.1.2.1, using the unfractionated TLE for derivatization.

2.3.4.2 Extraction of lipids from potsherds for radiocarbon determinations

Sherds containing lipid concentrations typically above 500 $\mu g.g^{-1}$ of sherd, were selected for radiocarbon determinations. A piece of 2 to 10 g of the potsherd was sampled, according to the lipid concentration and size of the remaining potsherd. The sherds were extracted in culture tube (I) using H_2SO_4/MeOH (4 % *v/v*, 3 x 8 mL, 70°C, 1 h). The supernatant was centrifuged (2500 rpm, 10 min) and combined into a second culture tube (II) containing double-distilled water (5 mL). The lipids were extracted with *n*-hexane (4 x 5 mL) and blown down to dryness at room temperature under a gentle nitrogen stream into a 3.5 mL vial. A procedural blank (same protocol without grounded clay in culture tube) was prepared and analysed alongside every batch of archaeological materials to assess whether contamination was introduced during the protocol. This protocol was an adaptation from the method described Correa-Ascencio and Evershed (2014) to improve the recovery of lipids extracted from a larger sized potsherd than those generally used for ORA.

The *n*-alkanols in the TLEs were derivatized with BSTFA (20 µL, 70 ºC, 1 h). Excess BSTFA was blown down under a nitrogen stream, then ~180 µL of *n*-hexane was added to obtain a concentration at 5 $\mu g.\mu L^{-1}$ before transfer to an autosampler vial for isolation in PCGC (Section 2.4.7) and graphitisation in an EA-AGE3 system (Section 2.4.8).

2.3.4.3 Pre-treatment of visible residues associated with pottery vessels

Approximately 20 mg of residue (see Chapter 7), scratched from the surface of the pot with a spatula, was weighed in a culture tube. First, the residues were treated with HCl (1 M, 10 mL, 1 h), then sonicated in fresh HCl (1 M, 10 mL, 15 min). The residue was then washed with MQ-water (4 x 10 mL) before sonication in MQ-water (10 mL, 5 min) until the water remained clear. The residues were treated again with HCl (1 M, 10 mL, 5 min), rinsed with MQ-water (2 x 10 mL) and then freeze-dried before being transferred to a tin or aluminium capsule for graphitisation with an EA-AGE3 system (Section 2.4.8; Brock *et al.* 2010).

2.3.4.4 Pre-treatment of archaeological seeds

Approximately 20 mg of seeds (see Section 4.4.2) were weighed into a culture tube. The seeds were pre-treated using an ABA (acid - base - acid) wash procedure (Section 1.3.3.3). The seeds were washed with HCl (1 M, 10 mL) until completion of the reaction with the carbonates. Then, they were washed with NaOH (0.2 M, 10 mL, 80 ºC, 20 min), and then with HCl (1 M, 10 mL, 1 h). In between each acid and base treatment the seeds were washed with MQ-water (3 x 10 mL). The washed seeds were freeze-dried before transfer into a Sn or Al capsule for graphitisation with EA-AGE3 equipment (Section 2.4.8; Brock *et al.* 2010). Preparation of lipids from seeds for CSRA dating of seeds was performed following the protocol Section 2.3.4.2.

2.3.4.5 Pre-treatment of archaeological bones

Approximately 300 mg of crushed bone (Chapter 7) were weighed into a culture tube and washed with HCl (0.5 M, 10 mL, until completion of the reaction with the carbonates) followed by a wash with NaOH (0.1 M, 10 mL, 30 min) and a second acid wash with HCl (0.5 M, 10 mL, 30 min). The bone collagen was rinsed with MQ-water (3 x 10 mL) in between each acid and base wash and centrifuged (3000 rpm, 5 min). The collagen was then gelatinised at pH 3 with HCl (0.001 M, 10 mL, 75 ºC, 20 h) and filtrated on glass wool filters before freeze drying (Brock *et al.* 2010; Section 1.3.3.3). The prepared collagen was transferred to an Al capsule and graphitised using EA-AGE3 equipment (Section 2.4.8). Additionally, $\delta^{13}C/\delta^{15}N$ analyses on the collagen were performed using an EA-IRMS instrument (Section 2.4.6).

2.3.4.6 Pre-treatment of archaeological shells

Surface cleaned shells (Chapter 7) were sonicated in MQ-water (5 mL, 5 min) until the water remained clear. When dried, the shells (~ 30 mg) were crushed roughly before the surface was acid etched (~20 %) with HCl (0.2 M, 10 mL), cleaned in MQ-water (3 x 10 mL) and dried in a drying cabinet (Section 1.3.3.3). The cleaned shells were then graphitised using a Carbonate Handling System, CHS-AGE3 equipment (Section 2.4.8; Brock *et al.* 2010).

2.4 Instruments

2.4.1 Gas chromatography (GC) and high-temperature GC (HT-GC)

GC analysis of TLEs (Section 2.3.2.1) for quantification was performed on a Hewelett Packard 5890 series II gas chromatograph or an Agilent Technologies 7890A GC. Helium was used as carrier gas at constant flow (2 $mL.min^{-1}$), and a flame ionisation detector (FID) used to monitor

column effluent. Lipids extracts (1 μL) were injected into a non-polar fused silica capillary column (50 m x 0.32 mm i.d., DB1 stationary phase (100 % dimethylpolysiloxane), 0.17 μm film thickness, Agilent technologies). The oven temperature program started with an isothermal hold at 50 ºC for 2 min, then the temperature was increased at 10 ºC.min^{-1} to 300 ºC and held for 10 min (Evershed *et al.* 1990).

GC analysis for quantification of isolated compounds via PCGC (Section 2.3.3) was performed on an Agilent Technologies 7890A GC instrument. The parameters were the same as above apart from the temperature program started with an isothermal hold at 50 ºC for 2 min, then the temperature increased at 20 ºC.min^{-1} to 300 ºC and held for 3 min.

HTGC analysis of TLEs (Section 2.3.2.2) for quantification was performed on an Agilent Technologies 7890A GC. Helium was used as carrier gas at constant flow (10 mL.min^{-1}), and a flame ionisation detector (FID) was used to monitor column effluent. Lipids extracts (1 μL) were injected into a non-polar fused silica column (15 m x 0.32 mm i.d., DB1 stationary phase, 0.1 μm film thickness, Agilent technologies). The oven temperature program started with an isothermal hold at 50 ºC for 2 min, then the temperature increased at 10 ºC.min^{-1} to 350 ºC and held for 10 min (Roffet-Salque *et al.* 2015). Data were acquired and processed by either the Chemstation control panel or Clarity software.

2.4.2 GC-mass spectrometry (GC-MS) and HT-GC-MS

GC-MS analysis of TLEs (Section 2.3.2.1) for molecular identification was performed on a Finnigan Trace MS quadrupole instrument coupled to a Trace GC, or on a Thermo Scientific ISQ LT single quadrupole GC-MS coupled to a Trace 1300, with manual or auto-sampling injections. The lipid extracts (1 μL) were introduced into a non-polar fused silica capillary column (50 m x 0.32 mm i.d., DB1 stationary phase, 0.17 μm film thickness, Agilent

Technologies). For TLEs analysis the oven temperature program started with an isothermal hold at 50 ºC during 2 min, then the temperature increased at 10 ºC.min^{-1} to 300 ºC and held for 10 min. The MS used electron ionization (EI) mode operating at 70 eV with a GC interface temperature of 300 ºC and a source temperature of 200 ºC. Acquisition used the total ion current (TIC) mode over the range *m/z* 50-650 Daltons at 8.3 scans.s^{-1} (Evershed *et al.* 1990). Screening for di-hydroxy fatty acid methyl esters (DHYAs, aquatic biomarkers) used selected ion monitoring (SIM) mode, monitoring *m/z* 159, 187, 215, 243, 259, 287, 315, 443, 459, 471, 487, 499 and 515 (for -COOMe derivatives instead of -COOTMS as published; Cramp and Evershed 2014).

In order to determine the presence of other aquatic biomarkers (APAAs and isoprenoid acids), TLEs (Section 2.3.2.1) were run on a polar column (60 m x 0.32 mm i.d., VF-23ms stationary phase (polydimethylsiloxane highly substituted with cyanopropyl groups), 0.15 µm film thickness, Agilent Technologies). The temperature program started with an isothermal hold at 70 ºC for 2 min, followed by a ramp at 10 ºC.min^{-1} to 220 ºC, then a ramp at 4 ºC.min^{-1} to 300 ºC and finally an isothermal hold for 10 min. Full scan mode *m/z* 50-650 and SIM mode, screening for the masses *m/z* 105, 262, 290, 318 and 346, were performed for the detection of APAAs (Cramp and Evershed 2014).

HTGC-MS analysis of wax esters (Section 2.3.2.2) was performed on the Thermo Scientific GC-MS system with manual injections. The TLEs (1 µL) were introduced into a non-polar fused silica column (15 m x 0.32 mm i.d., DB1 stationary phase, 0.1 µm film thickness, Agilent technologies). For wax esters analysis oven temperature program started with an isothermal hold at 50 ºC for 2 min, then the temperature increased to 280 ºC at 10 ºC.min^{-1} then increased to 380 ºC at 25 ºC.min^{-1} and held for 5 min. The data were acquired using TIC mode over the range *m/z* 50-950 Daltons at 8.3 scans per second (Roffet-Salque *et al.* 2015).

Data were processed with XCalibur software, and the peaks were identified using the NIST mass spectral library.

2.4.3 GC-combustion-isotope ratio MS (GC-C-IRMS)

The GC-C-IRMS analyses on $C_{16:0}$ and $C_{18:0}$ FAs (for identification of the source of animal fats) was performed on an Agilent Technologies 7890A, coupled via an IsoPrime GC5 combustion interface (CuO and silver reactor, 850 ºC) to an IsoPrime 100 mass spectrometer. The FAME extracts (1 µL) were injected into a non-polar column (50 m x 0.32 mm i.d., DB1 stationary phase, 0.17 µm film thickness, Agilent technologies). The GC oven temperature was held for 2 min at 40 ºC and increased to 300 ºC at 10 ºC.min^{-1} and held for 10 min. The MS used EI at 70 eV and had three Faraday cups collecting for the masses *m/z* 44, 45 and 46. Data were acquired and processed by the IonVantage software (Copley *et al.* 2003).

2.4.4 Nuclear magnetic resonance (NMR) spectroscopy

NMR was used to identify and quantify background C contamination from PCGC instrument (Section 2.3.3; Chapter 3). Standard 1D ^{1}H spectra (25 ºC, 15 ppm spectral width, 65 536 complex points, 3.12 s per scans, 1 s interscan delay, 5120 scans, 5 h 55 min) were recorded using a Brucker Advance II HD 700 MHz NMR instrument equipped with a 1.7 mm microcryoprobe, to ensure proper sensitivity. The spectra were referenced to the residual solvent signal (^{1}H, δ 7.26 ppm). An SGE gas-tight syringe was used to fill 1.7 mm NMR tubes with 50 µL of the PCGC isolated compounds concentrated at 1 µg.µL^{1}. NMR analysis of the solvent was performed to confirm its purity and eliminate TMS (tetramethylsilane, commonly added to NMR solvents) as a possible source of interference.

The spectra were processed and analysed in MestreNova v 9. A multiple point background correction was performed by subtraction of a cubic spline function, on a sample-by-sample basis, adjusted by adding manual points to achieve a flattened area adjacent to the peaks used for quantification. Phase correction was performed manually using the peak at 1.28 ppm as a pivot position. The spectra were normalised to the peak at 1.28 ppm. Integration was performed using a peak-by-peak calculation method, with the cyclic poly(dimethyl siloxane) peaks requiring manual integration.

2.4.5 GC/quadrupole – time of flight MS (GC/Q-TOFMS)

GC/Q-TOFMS analyses for the identification of exogenous C (Section 2.3.3, Chapter 3) were performed on an Agilent Technologies 7890b GC instrument coupled to an Agilent Technologies 7200 Accurate Mass Q-TOF MS device. Isolated compounds by PCGC (1 μL) were injected into a non-polar fused silica capillary column (50 m x 0.32 mm i.d., DB1 stationary phase (100 % dimethylpolysiloxane), 0.17 μm film thickness, Agilent Technologies). For cyclic poly(dimethylsiloxanes) analysis the temperature program started at 50ºC and increased to 300 ºC at 30º min^{-1}. Data were acquired over the range of *m/z* 50-1200 Da, from 5-16 min, to capture the elution window of the cyclic poly(dimethylsiloxane) oligomers and avoid saturation of the instrument with FAMEs and IS. Data were processed using the NIST database.

2.4.6 Elemental analyser– IRMS (EA-IRMS)

The $\delta^{13}C$ analysis of methanol used for the derivatisation of FAs (Sections 2.3.2.1, 2.3.4.2) was carried out using a Flash EA 1112 series coupled to a Thermo Finnigan Delta^{plus} XP to allow correction of $\delta^{13}C$ values on individual FAs. The methanol aliquots were manually injected (0.2 μL) and measured in quadruplicate. Liquid standards ERM EtOH ($\delta^{13}C$ = -26.91 ‰) and

Acros ETBE ($\delta^{13}C$ = -19.73 ‰) were used for calibration and Bayensoil ETBE ($\delta^{13}C$ = -26.06 ‰) was used as a quality control.

Bulk $\delta^{13}C$ and $\delta^{15}N$ analysis of collagen for acceptability (Chapter 7) and reference fatty acids (Chapter 4) were performed on the same instrument. The collagen extracts and FAs (3 mg and 0.25 mg, respectively) were weighed into Sn capsules before loading onto the instrument and analysing in triplicate. Standards materials FRIMS phenacetin ($\delta^{13}C$ = -26.67 ± 0.13, $\delta^{15}N$ = -8.36 ± 0.04 ‰) and FRIMS 209-1 Hemp ($\delta^{13}C$ = -28.39 ± 0.03, $\delta^{15}N$ = -4.61 ± 0.04 ‰) were used as calibration and FRIMS 203-1 Chitin ($\delta^{13}C$ = -22.08 ± 0.05, $\delta^{15}N$ = -40.81 ± 0.06 ‰) was used as a quality control for the collagen. Standard FRIMS sugar ($\delta^{13}C$ = -11.64 ± 0.25 ‰) and FRIMS 4-nitroacetanide ($\delta^{13}C$ = -32.95 ± 0.32 ‰) were used as calibration standards and FRIMS magnesium stearate ($\delta^{13}C$ = -30.31 ± 0.089 ‰) as a quality control for the reference FAs.

2.4.7 Preparative capillary GC (PCGC)

The PCGC (Eglinton *et al.* 1996; Chapter 3), used for FAs isolation, consisted of a Hewlett Packard 5890 series II gas chromatograph coupled to a Gerstel Preparative Fraction Collector by a heated transfer line. The GC was equipped with a column with a 100% poly(dimethyl siloxane) stationary phase (Rxi-1ms, 30 m x 0.53 mm i.d., 1.5 μm film thickness, Restek,). Helium was used as a carrier gas at a constant pressure of 10 psi. For FAME standards, the GC oven started with an isothermal hold at 50 °C for 2 min before increasing to 300 °C at 10 °C.min^{-1} and held for 2 min. To separate FAMEs from archaeological materials, the GC oven started with an isothermal hold at 50 °C for 2 min, increased to 200 °C at 40 °C.min^{-1}, then increased to 270 °C at 10 °C.min^{-1} and finally increased to 300 °C at 20 °C.min^{-1} and held for 8.75 min for the elution of all compounds in the TLE. FAMEs (from standard solutions and

archaeological materials) at a concentration of ca. 5 μg C.μL^{-1} were injected (1 μL per run), separated and trapped 40 times per trapping sequence. One percent of the GC column effluent flows to the flame ionization detector (FID), whilst the remaining 99% passes via a transfer line into the PFC, both heated to 300 °C. Compounds were isolated based on their retention times. Trapping 'windows' were typically 1 min for FAME standards and blank injections, but those for archaeological materials were adjusted slightly to avoid co-isolation of other closely eluting compounds. The $C_{16:0}$ FAMEs were isolated in trap '$TC_{16:0}$' and the $C_{18:0}$ FAMEs were isolated in trap '$TC_{18:0}$'. Trap, 'T_W' was used as the waste trap and all column effluent passed through this trap outside the trapping windows.

Processing standards and blanks for radiocarbon analysis were prepared by performing trapping sequences whereby only solvent was injected, but the trapping 'windows' were the same as for real lipid extracts in order to mirror the concentrations of any exogenous C introduced by this process. Blank material (phthalic anhydride) and IAEA C7 (age approximating the potsherds dated; Le Clercq *et al.* 1997) were added to individual capsules after the transfer of the trap contents and analysed alongside isolated compounds. These were compared and used instead unprocessed standard for AMS (Section 2.4.9) for each batch containing pots. Each trap containing sample was individually wrapped in foil before compound recovery. Between each trapping sequence the GC column was backed (300 ºC, 15 min), the autosampler syringe sonicated in ethyl acetate (10 min) then DCM (10 min), the wash ethyl acetate solvent replaced, and PFC capillaries cleaned using the heat gun method presented in Chapter 3.

2.4.8 Automated graphitisation equipment (AGE)

Organic materials (FAMEs and collagen) were combusted to CO_2 in O_2 using a Vario Microcube Elemental Analyser (EA, Elementar). The shells (carbonated material) were treated in H_2 with H_3PO_4 (1 mL, 70 ^oC) using a Carbonate Handling System (CHS, Ionplus; Wacker *et al.* 2013b) to generate CO_2. Resulting CO_2 was adsorbed on Zeolite traps then released to reaction tubes heated at 450 ºC using the Automated Graphitisation Equipment (AGE 3, Ionplus; Wacker *et al.* 2010b). The CO_2 was reduced to graphite under H_2 (580 ºC, 2 h, 420 mbar) on a pre-conditioned iron catalyst. A Pneumatic Sample Press (PSP, Ionplus) was used to press the graphitised samples into Al targets.

2.4.9 Accelerator mass spectrometer (AMS)

All ^{14}C determinations were performed at the BRAMS (Bristol Accelerator Mass Spectrometer) facility which is equipped with a mini radiocarbon dating system (BRIS-MICADAS) instrument (Ionplus*;* Synal *et al.* 2007). Graphite targets were ionised in a caesium sputtered ion source and accelerated to a potential of 200 kV for the separation of ^{12}C, ^{13}C and ^{14}C isotopes. Collection of the ^{12}C and ^{13}C stable isotope into faraday cups to measure $\delta^{13}C$ was assured for the correction of $^{14}C/^{12}C$ value for fractionation (see Section 1.3.2; Wacker *et al.* 2010a). Data were acquired using BATS software.

For each magazine, standards of known age (Table 2-1), were measured at the same time to validate the pre-treatments and measurements from the AMS (e.g. Rozanski *et al.* 1992; Gulliksen and Scott 1995). Blank materials (e.g. phthalic anhydride) were measured to assure the background correction and Ox II normalisation (Sections 1.3.2, 2.2.1). When possible, standards materials of the same nature/age were pre-treated together with unknown age archaeological materials to assure no contamination was introduced during the pre-treatment

procedure (processed standards; Table 2-1). Each magazine containing archaeological materials reported in the thesis showed valid values for known-age standards after normalisation and background corrections suggesting no obvious contamination during the pre-treatment and analyses. Only potsherds with sample sizes below 100 µg which counting statistic failed the χ^2 test at the 5% level were indicated as such and considered not reliable.

2.5 Data processing

2.5.1 Lipid residue analysis

Quantification of lipids by GC (Section 2.4.1) was carried out using the internal standard (*n*-tetratriacontane; 20 µL) added at the first stage of the extraction protocol. The concentration of lipids in the TLE was calculated based on the peak areas in the gas chromatogram using Equation 2-1:

$$C_{lipids} = \frac{(100 - A_{IS} - A_{cont}) * m_{IS}}{A_{IS} * m_{sherd}}$$

Equation 2-1

Where C_{lipids} = lipid concentration ($\mu g.g^{-1}$)
A_{IS} = peak area of the internal standard (%)
A_{cont} = peak area of contaminants in appreciable concentration (%)
m_{IS} = mass of the internal standard added (µg)
m_{sherd} = mass of powdered potsherd extracted (g)

The raw $\delta^{13}C$ values of FAs obtained by GC-C-IRMS (Section 2.4.3) analyses were corrected for the C atoms added during the methylation of the fatty acids. The correction of the $\delta^{13}C$ value was performed using the mass balance Equation 2-2 (Rieley 1994):

$$\delta^{13}{}_{FA} = \frac{No.C_{FAME} * \delta^{13}{}_{FAME} - \delta^{13}{}_{MeOH}}{No.C_{FA}}$$

Equation 2-2

Where $\delta^{13}C_{FA}$ = $\delta^{13}C$ value of the original fatty acid (‰)
$\delta^{13}C_{FAME}$ = measured $\delta^{13}C$ value of the FAME (‰)
$\delta^{13}C_{MeOH}$ = measured $\delta^{13}C$ value of MeOH used for the methylation (‰)
$No.C_{FAME}$ = total number of C atoms in the FAME
$No.C_{FA}$ = total number of C in the original fatty acid

2.5.2 Quantification exogenous C during the PCGC procedure

2.5.2.1 Quantification of single compounds isolated by PCGC

The quantification of single compounds isolated by PCGC (Sections 2.4.1, 2.4.7) was performed by the introduction of a standard (*n*-tetratriacontane) after the isolation of the FAs. The amount of trapped FAME (and potential contaminants) was calculated based on the peak areas in the gas chromatogram using Equation 2-3:

$$m_{compound} = \frac{A_{compound} * m_{IS}}{A_{IS}}$$

Equation 2-3

Where $m_{compound}$ = mass of the isolated compound by PCGC ($\mu g.g^{-1}$)
m_{IS} = mass of the internal standard (µg)
A_{IS} = peak area of the internal standard (%)
$A_{compound}$ = peak area of the isolated compound by PCGC (%)

2.5.2.2 Calibration of the NMR instrument and quantification of exogenous C

In order to quantify the amount of column bleed collected in the traps together with the FAMEs during PCGC (Sections 3.4, 3.5), a calibration curve was generated covering (Section 2.3.3.2). The concentration of the standard solutions in $mg.mL^{-1}$ were converted into the mass of C of the compounds using Equation 2-4.

$$mC_x = \frac{[x] * V_x * M_C * No.C}{M_x}$$

Equation 2-4

where	x	=	either the $C_{18:0}$ FAME or the hexamethylcyclotrisiloxane
	mC_x	=	carbon atom, mCx is the mass of C in the compound (mg)
	[x]	=	concentration ($mg.mL^{-1}$)
	V_x	=	volume (mL)
	M_C	=	molar mass of C ($mg.mol^{-1}$)
	M_x	=	molar mass ($mg.mol^{-1}$)
	No.C	=	number of C atoms in the molecule

Based on the mass of C trapped, the NMR peak areas and the calibration curve slope, the amount of carbon from the column bleed was determined using Equation 2-5. The same equation was used for quantification of any contaminant arising from the incomplete removal of solvent after recovery of compounds in the G-traps.

$$mC_{cont} = \frac{A_{cont}}{A_{FAME}} * \frac{mC_{FAME}}{S}$$

Equation 2-5

Where	mC_{cont}	=	mass of C from exogenous contamination
	mC_{FAME}	=	mass of C from the FAME
	A_{cont}	=	peak area of exogenous contamination
	A_{FAME}	=	peak area of FAME
	S	=	slope of the linear calibration (= 25.843)

The shift in years to older age associated with the introduction of contamination from infinite age C can be calculated based on Equation 2-6 (rearranged from Bowman 1990).

$$\Delta Age = -8033 * \ln(1 - f_{cont})$$

Equation 2-6

Where	ΔAge	=	shift from the real age of the material (y)
	f_{cont}	=	fraction of exogenous contamination

2.5.2.3 Determination of the amount of cross-contamination

The amount of residual compound from cross-contamination (see Section 3.6) associated with an isolated compound was calculated using Equation 2-7.

$$f_{cont} = \frac{(F^{14}C_{measured} - F^{14}C_{compound})}{(F^{14}C_{cont} - F^{14}C_{compound})}$$

Equation 2-7

Where f_{cont} = fraction of exogenous contaminant
$F^{14}C_{measured}$ = fraction modern measured
$F^{14}C_{compound}$ = fraction modern of the isolated compound
$F^{14}C_{cont}$ = fraction modern of the exogenous contaminant

2.5.3 Radiocarbon analysis

The tables reporting radiocarbon determinations in this thesis give both the fraction modern ($F^{14}C$) and the conventional radiocarbon age with associated analytical errors. In the discussion, the fraction modern was used for modern materials (i.e. post bomb peak) and the conventional radiocarbon age was used for archaeological materials.

2.5.3.1 Correction of fraction modern from the methyl group

The ^{14}C determinations on the isolated FAMEs were corrected for the carbon atoms added during the methylation of the FAs (Section 2.3.4.2). The correction was performed using a mass balance method described in Equation 2-8 (Stott *et al.* 2003):

$$F^{14}C_{FA.1} = \frac{No.C_{FAME} * F^{14}C_{measured}}{No.C_{FA}}$$

Equation 2-8

Where $F^{14}C_{FA.1}$ = fraction modern of the original FA
$F^{14}C_{measured}$ = fraction modern of the measured FAME
$No.C_{FAME}$ = total number of C atoms in the FAME
$No.C_{FA}$ = total number of C in the original FA

A further correction of the standard FAs (Section 3.3.3), could be made to correct for the fractionation effect which may occur during the derivatization of the FAs using Equation 2-9 (Stott *et al.* 2003):

$$F^{14}C_{FA.2} = F^{14}C_{FA.1} * \left(\frac{1 + \left[\frac{-25 + \delta^{13}C_{FAME}}{1000} \right]}{1 + \left[\frac{-25 + \delta^{13}C_{FA}}{1000} \right]} \right)$$

Equation 2-9

Where $F^{14}C_{FA.2}$ = fraction modern of the original FA corrected for fractionation
$F^{14}C_{FA.1}$ = fraction modern of the original FA corrected by mass balance
$\delta^{13}C_{FA}$ = $\delta^{13}C$ value of the original FA (‰)
$\delta^{13}C_{FAME}$ = $\delta^{13}C$ value of the FAME (‰)

Where the $C_{16:0}$ and $C_{18:0}$ FAs were isolated in the same traps, the ^{14}C determinations were corrected from the carbon atoms added during the methylation of the fatty acids as described in Equation 2-10. The fraction of the two fatty acids collected in the traps was determined based on the peak areas in the gas chromatogram.

$$F^{14}C_{FA_{comb}} = (\frac{17}{16} * f_{c_{16:0}} + \frac{19}{18} * f_{c_{18:0}}) * F^{14}C_{measured}$$

Equation 2-10

Where $F^{14}C_{FAcomb}$ = fraction modern of the original FAs combined in the trap
$F^{14}C_{measured}$ = fraction modern measured
$fc_{16:0}$ = fraction of $C_{16:0}$ collected in the trap
$fc_{18:0}$ = fraction of $C_{18:0}$ collected in the trap

2.5.3.2 Conversion of fraction modern to uncalibrated radiocarbon age

The fraction modern $F^{14}C$ values were converted to the conventional radiocarbon age BP using Equation 2-11:

$$Age_{FA} = -8033 * ln(F^{14}C_{FA})$$

Equation 2-11

Where Age_{FA} = age of the FA (BP)
$F^{14}C_{FA}$ = corrected fraction modern of the FA

2.5.3.3 Comparison and combination of uncalibrated ^{14}C determinations

One measured ^{14}C age χ, is given with a quoted error (or analytical uncertainty) s. A measurement with a 1σ uncertainty range ($\chi \pm s$) corresponds to a 68% confidence interval and in the 2σ uncertainty range ($\chi \pm 2s$) to a 95 % confidence interval (Scott *et al.* 2007a).

To evaluate if two measured ^{14}C ages, χ_1 and χ_2 with the analytical uncertainty associated s_1 and s_2 had the same true age $\chi_1 - \chi_2 \pm 2\sqrt{{s_1}^2 + {s_2}^2}$ was calculated. If it includes 0 (i.e. $\chi_1 - \chi_2 < 2\sqrt{{s_1}^2 + {s_2}^2}$), then the measurements are identical within a 2σ range (Scott *et al.* 2007a).

A statistical T-test, also known as a χ^2 test for n-1 degrees of freedom (following Equation 2-12), was used to assess if n radiocarbon measurements were statistically indistinguishable and could be combined (Ward and Wilson 1978). The value should be smaller than a critical value given in statistical tables (usually the value $\chi^2_{0.05}$ for a 95% confidence) for n-1 degrees of freedom, to pass the test. The results were reported as T', T'(5%) and υ respectively for the χ^2 value of the measurements, the $\chi^2_{0.05}$ value at 5% from statistical tables and the degree of freedom (Ward and Wilson 1978; Scott *et al.* 2007a).

$$T' = \sum_1^n \left(\frac{\chi_i - \overline{X}_p}{s_i}\right)^2$$

Equation 2-12

Where	T' (or χ^2)	=	statistical test
	n	=	number of ^{14}C measurements
	$\overline{X}_p$	=	weighted average of the ^{14}C measurements
	χ_i	=	one ^{14}C measurement ($F^{14}C$ or Age BP)
	s_i	=	analytical uncertainty associated with the measurement i

with calculation of the weighted average of using Equation 2-13:

$$\overline{X}_p = \frac{\sum \chi_i / {s_i}^2}{\sum 1/{s_i}^2}$$

Equation 2-13

Where $\overline{X}_p$ = weighted average
χ_i = one individual ^{14}C measurement ($F^{14}C$ or Age BP)
s_i = analytical uncertainty associated with the ^{14}C measurement χ_i

And the calculation of error associated with the weighted average using Equation 2-14:

$$\sigma(\overline{X}_p) = \sqrt{\frac{1}{\sum 1/{s_i}^2}}$$

Equation 2-14

Where $\sigma(\overline{X}_p)$ = error associated with the weighted average
n = number of ^{14}C measurements
s_i = analytical uncertainty associated with the ^{14}C measurement χ_i

2.5.3.4 Conversion of uncalibrated age into a calibrated calendar age

The uncalibrated dates (BP) were converted into calendar age using the OxCal software v4.2 or v4.3 using the function *R_Date* (Bronk Ramsey 2009). All data were calibrated against the IntCal13 calibration curve for terrestrial organisms and Marine 13 calibration curve for marine organisms (Reimer *et al.* 2013). Potsherds from Samburu post 1950 (see Section 6.3) were calibrated against Bomb 13 NH3. The 68 % (1σ) and 95 % (2σ) confidence intervals were given together with the probability distribution of an event to occur at a particular time.

When two radiocarbon measurements of the same material were identical (within error), they were combined prior to calibration using the weighted average and weighted error. For two FAs from the same pottery vessels the uncertainty associated with the combined measurements were not calculated by the same method as described in Section 2.5.3.3. This is because any

analytical error on the 2 FAs are linked, thus a conventional combination of measurements would underestimate the true error. The combined error was calculated using Equation 2-15.

$$\sigma_{true} = \sqrt{(\overline{X}_c * Ss)^2 + {s_c}^2}$$

Equation 2-15

Where σ_{true} = error associated with the combined measurements of the FAs
Xc = weighted average with AMS error only
Ss = sample scatter factor
s_c = AMS error

2.5.3.5 Evaluation of calibrated dates by chronological modelling

To test the reliability of the dates produced using this protocol, it was decided to use pottery vessels from well-dated sites, with a sequence of calibrated dates. For example, at the Sweet Track, where the age was known by dendrochronological dating (Section 4.4.1) the function *D_sequence* in OxCal (Bronk Ramsey *et al.* 2001) was used to compare the calibrated radiocarbon dates on pottery lipids with those included in the IntCal13 calibration curve for the relevant decade. The results were given with A_{comb}, A_n and *n* values. A_{comb} corresponds to the overall agreement (in %), which was expected to be as close as possible to 100 % for a good agreement of measurements, A_n to the threshold of acceptability of the A_{comb} value and *n* to the number of ^{14}C measurements.

For sites dated by conventional ^{14}C dates presenting a modelled sequence (Bronk Ramsey 1995; Sections 4.4.3, 4.4.4, 5.5), the dates generated from pottery vessels were included in the pre-existing model. The chronological models using Bayesian statistics and including radiocarbon dates on pottery vessels were performed by Professor A. Bayliss in OxCal v4.2 (Bronk Ramsey 2009), following the codes in previously published sequences (Marshall *et al.* 2014; Marciniak *et al.* 2015; Denaire *et al.* 2017). Dates on pottery vessels were included in a position defined by the stratigraphy/seriation at the site. Such a model should have an

agreement A_{model} the closest to 100 % with a threshold of 60% (Bronk Ramsey 1995 Bronk Ramsey 2009). The same applies to individual agreement A on radiocarbon dates to fit with the model.

For LBK pottery vessels from unknown age sites, where dates were required in order to ascertain the beginning of dairying practices, a model was produced using the *Sequence_* function and compared to the available models for the formative LBK groups and the Alsatian LBK sequence (Chapter 6; Jakucs *et al.* 2016; Denaire *et al.* 2017)

2.5.3.6 Calculation of marine reservoir offsets

The analysis of pottery vessels from the site of Bornais (Chapter 7) required calculation of the local deviation to the reservoir effect (ΔR) to allow correction for the MRE in archaeological pottery vessels. Radiocarbon dates were produced on references materials (i.e. terrestrial mammal bones, fish bone and shells) from the same archaeological contexts of the potsherds and subjected to a χ^2 test on a context by context basis to detect outliers. Samples that were measured twice were combined before ΔR calculation (Ascough *et al.* 2007b). ΔR was calculated for every pair of terrestrial/marine organisms (excluding the statistical outliers) using the software CALIB v7.1 and the online method (interpolation of curves) to calculate ΔR (Stuiver *et al.* 2018; Reimer and Reimer 2016). The weighted average of individual ΔR values obtained for each paired terrestrial/marine organism (excluding statistical outliers) was undertaken to obtain the final ΔR. The uncertainty associated with ΔR was calculated following Equation 2-16 (Russell *et al.* 2011).

$$\sigma = \sqrt{(\sigma(\overline{X}_p)^2 + {S_{dev}}^2)}$$

Equation 2-16

Where σ = error associated with ΔR_{final}
$\sigma(\overline{X}_p)$ = error associated with the weighted average of ΔR values
S_{dev} = standard deviation associated with ΔR values

2.5.3.7 Calculation and calibration of the proportion of aquatic products

Two methods were used to calculate the percentage of marine products in pots (see Chapter 7). The first one, used as a reference is based on the weighted average age of terrestrial organisms, the weighted average age of marine organisms and the age of pottery lipids from the same context/phase the proportion of aquatic/terrestrial products in a pottery vessel was evaluated using Equation 2-17. The error associated corresponds to the propagation of analytical errors.

$$\%_{aqua} = \frac{(Age_{pot} - Age_{terres})}{(Age_{aqua} - Age_{terres})} * 100$$

Equation 2-17

Where $\%_{aqua}$ = proportion of aquatic commodity in the pot (%)
Age_{pot} = age obtained from pottery lipids (BP)
Age_{terres} = weighted average age of the terrestrial organism (BP)
Age_{aqua} = weighted average age of the aquatic organism (BP)

The second one calculates the percentage of aquatic resource using the same equation but with $\delta^{13}C$ values on individual $C_{16:0}$ and $C_{18:0}$ FAs. Data points from UK reference animals (Copley *et al.* 2003; Cramp and Evershed 2014) were used as end-members (see Section 7.5.2.1) and error calculated using the propagation of analytical error. The weighted average of percentages calculated on both FAs was accepted as the final value with the error calculated using Equation 2-16.

The radiocarbon age from mixed aquatic/terrestrial products was calibrated in OxCal v4.3 (Bronk Ramsey 2009) using the *Marine/mixed curve* function. It uses the IntCal 13 and Marine 13 calibration curves (Reimer *et al.* 2013), ΔR calculated for the site and the percentage of mixed resources calculated for the calibration of one radiocarbon measurement.

Chapter 3.

Methodological considerations for CSRA

Chapter 3. Methodological considerations for CSRA

NB: The quantification of exogenous carbon from PCGC (Sections 3.1.2 and 3.4) and the newly developed trap design plus cross-contamination removal (Sections 3.1.3, 3.5 and 3.6) are published in Analytical Chemistry, 2017, 89, 13, 7090 and 2018, 90, 18, 11025, respectively.

3.1 Challenges for accuracy and high precision in CSRA

Preparative capillary gas chromatography (PCGC) was used previously by Stott *et al.* (2001, 2003) and Berstan *et al.* (2008) in the first attempts at dating lipids preserved in pottery vessels. Despite some promising results, the dates obtained from lipids isolated from pots lacked accuracy, by several hundreds of years often showing high variability of the dates on the two FAs isolated from the same vessel (statistically non-identical results). Furthermore, the dates obtained did not correlate well with the dates of associated materials. The poor dating accuracy was likely due to exogenous C derived from the sample preparation procedure and/or the PCGC contaminating the analytes (Ziolkowski and Druffel 2009). The aforementioned studies, however, provided important groundwork for the development of the technique for CSRA of pottery lipids. Herein, PCGC is used to isolate selected biomarkers, i.e. $C_{16:0}$ and $C_{18:0}$ fatty acids, deriving from the degradation of animal fats, and develop the methodology for a new, reliable and accurate method of dating archaeological pottery vessels.

3.1.1 Isolation of fatty acids methyl esters by PCGC

3.1.1.1 Sample size

Typically, 1 mg of C is required for radiocarbon dating but it can be difficult to obtain such a large amount of C from lipids preserved in pottery vessels. Today, advances in sample

preparation and AMS techniques means that smaller sizes (a few micrograms) can be sufficient to provide radiocarbon dates (Santos *et al.* 2007, 2010; Cersoy *et al.* 2017). With an AGE 3 instrument (used in this thesis; Wacker *et al.* 2010b), amount of C present in a material below 100 μg of C is difficult to generate and measurements will require analysis at a small current and potentially present higher background leading to less precise and accurate ^{14}C determinations. It is possible to directly date the material using the CO_2 method although this requires a gas ion source (Bronk Ramsey *et al.* 2004a; Wacker *et al.* 2013a) but the precision of such measurements (usually ca. 60-100 years) would be too low for archaeological applications. In the case of dating archaeological pottery vessels high precision (i.e. below 30 years error) ^{14}C measurements are required for their conversion to calendar ages. The definition of C sample size to be isolated by PCGC is therefore highly important as this will directly affect the error on the measurements.

3.1.1.2 Length of a trapping sequence

The method used by Stott *et al.* (2003) consisted of injecting lipid extracts through a 0.5 μm thickness column, which allowed the isolation of lipid extracts over a 45 min temperature program. However, several days of isolation (sometimes up to a week) per sherd extract was necessary to trap sufficient amounts of C (> 200 μg) for AMS analysis. Obviously, this method was extremely time-consuming and would consequently only allow limited numbers of lipid extracts to be isolated. One aim of this thesis was to develop a methodology which would allow shorter preparation times, in order that the procedure could be used for rapid isolation of compounds from TLEs, making it suitable for dating large numbers of archaeological samples.

3.1.1.3 Correction of the extra C added during derivatisation

During their extraction from the clay, the FAs are derivatized to fatty acid methyl esters (FAMEs), which adds an extra C group that requires correction. Stott *et al.* (2003) used a mass balance method, introduced by Eglinton *et al.* (1996), to correct the contribution of the methyl group but also added a second correction which took into account any fractionation occurring during methylation. The $\delta^{13}C$ value of the FAME obtained from the AMS instrument was used to calculate the $\delta^{13}C$ value of the isolated FA using a mass balance calculation (Section 2.5.3.1). The $\delta^{13}C$ value obtained from an AMS is, however, less precise for stable C isotope ratio measurements than IRMS instruments (ca. 2 ‰ for an AMS against 0.1 ‰ for an IRMS; McIntyre *et al.* 2017). The validity of the correction for fractionation during the methylation was also never tested and require investigation to understand the effects of such corrections.

3.1.2 Contamination associated with degradation of the column stationary phase

3.1.2.1 Nature and degradation of column stationary phase

The most widely used GC column for PCGC analysis, and that used in this project is coated with poly(dimethylsiloxanes; PDMS; Figure 3-1). The polymer coating the column (i.e. PDMS stationary phase) is susceptible to thermal degradation through extended heating to high temperatures (ca. 300 ^{o}C) in the GC oven (Schomburg *et al.* 1978; Grob and Grob 1982). The cyclic degradation products of the polymer typically released are the n = 3 and n = 4 cyclic oligomers of the monomer unit (-[$Si(CH_3)_2$-O]$_n$-), with the possibility of higher homologues up to n = 7 (Aleksandrova *et al.* 1968, Thomas and Kendrick 1969). Therefore, during PCGC the stationary phase releases carbon-containing degradation products (‘column bleed’), which are potential contaminants of the trapped compounds. The monomeric precursors used to synthesise the polymeric stationary phases commonly petroleum derived (i.e. radiocarbon

dead; Chojnowski and Cypryk 2000) which means that the impact of column bleed on the isolated FAMEs is to shift the radiocarbon determinations towards 'older' values. Infinite age radiocarbon contamination is considered significant at the part per thousand level (1 ‰, i.e. ~ 8 years; Bowman 1990).

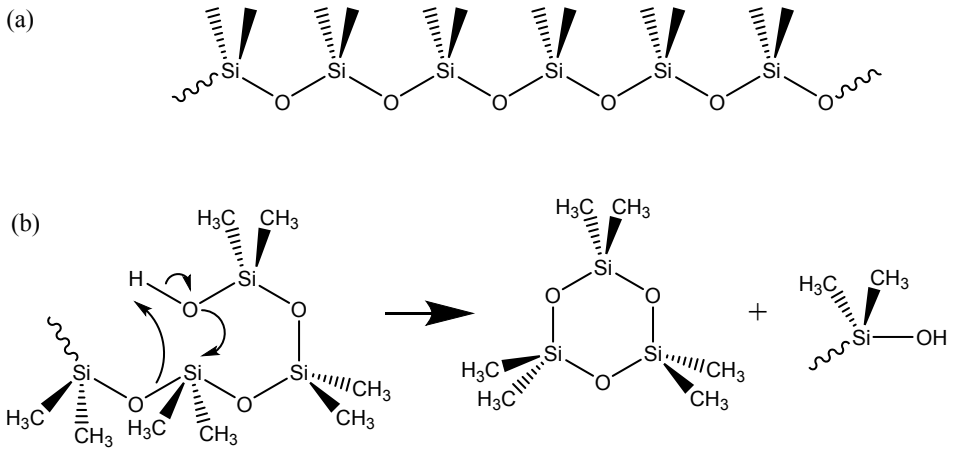

Figure 3-1: (a) Structure of poly(dimethyl siloxane) polymer. (b) Degradation mechanism under heat (adapted from Grassie and Macfarlane 1978).

3.1.2.2 Reducing and quantifying column degradation products

Several approaches have been considered to identify, limit and correct for the effects of 'column bleed' from the GC column. This phenomenon was considered in the first use of the CRSA method by Eglinton *et al.* (1996), wherein they suggested using a thinly coated column with low bleed characteristics. Stott *et al.* (2003), attempted to determine the column bleed concentration via preparation of chromatographic blanks, which involved collecting the entire eluent of a GC run. The blanks contained insufficient C for radiocarbon analysis (~0.9 µg) thus, the effect of column bleed on CSRA determinations was assumed to be insignificant. Later, Ziolkowski and Druffel (2009) generated blanks based on 400 dry injections and trapping 7 min retention time 'windows' then normalising the amount of exogenous C to 50 injections. This assumes a column degradation rate independent of time and temperature. However, it is

known that that the release of PDMS from GC columns increases with temperature. A further approach (and probably the most effective one) to assess the effect of column bleed involved the isolating of reference compounds of known modern age then investigating shifts in ^{14}C content by radiocarbon analysis (Zencak *et al.* 2007; Ziolkowski and Druffel 2009; Coppola *et al.* 2013). The influence of column bleed was estimated from deviations in the ^{14}C content of reference materials compared to those of dry injections, i.e. blanks. In summary, the direct characterisation and quantification of the small quantities of contaminants in target compounds isolated by PCGC, that could potentially affect high precision and accurate ^{14}C determinations, is extremely challenging. The above studies therefore highlight the need for a new approach for assessing directly analyte purity in compound-specific ^{14}C determinations.

3.1.3 Other sources of contamination associated with the isolation procedure

3.1.3.1 Incomplete removal of solvent

Compounds isolated by PCGC into the commercially available glass traps are recovered by back-flushing the trap with an organic solvent followed by removal of the washing solvent under a gentle stream of N_2. The compounds isolated by PCGC are apolar, hence, their affinity for organic solvents could result in the incomplete removal of residual transfer solvent. The low quantities of analyte trapped, combined with their often relatively high volatilities, mean that it is undesirable to blow analytes down too strongly or for too long, as this could result in evaporative losses. Considering that any exogenous C present at the per mil level would have a significant effect on the determined radiocarbon date of an isolated compound, it is conceivable that this could represent a significant source of contaminating exogenous C in an isolated compound. Indeed, although they were unable to identify or quantify any residual solvent using high resolution GCMS or shifts in $\delta^{13}C$ values, in 1996 Eglinton *et al*. noted that

"Incomplete removal of solvent prior to combustion is the major potential source of carbon contamination" in compounds isolated by PCGC. Surprisingly, the potential for organic solvents, used to manipulate analytes post-trapping, to persist after drying of compounds is not something that appears to have been systematically investigated.

3.1.3.2 Memory effect or cross-contamination

A further challenge recognized in the radiocarbon determination of organic compounds isolated by PCGC is cross-contamination between trapping runs (Ziolkowski and Druffel 2009). Strategies for avoiding cross-contamination involve 'washing' the entire system by performing repeated injections (10x) of aliquots of the new extract, discarding the resulting isolates and replacing the 'used' traps with clean ones (Ziolkowski and Druffel 2009; Coppola *et al.* 2013; Cisneros-Dozal *et al.* 2016). This practice is undesirable as it constitutes loss of precious analyte especially given that isolating and trapping enough C is one of the major challenges in CSRA. Furthermore, the efficacy of this practice has not been rigorously tested in the literature. It is most likely that any cross-contamination would occur as a result of compounds from earlier trapping sequences becoming condensed at 'cold spots' (where the fused silica capillaries protrude from the heated sections of the PFC unit and enter the unheated glass traps) in the PCGC system but are re-mobilized, contaminating the subsequently trapped compound. Although this factor is well-known (Ziolkowski and Druffel 2009), previous research has only offered time-consuming solutions which involve significant losses of materials.

3.2 Aims and objectives

The aim of this chapter was to develop a method which will allow the accurate and reliable dating of lipids extracted from archaeological pottery vessels, on a routine basis, by compound-

specific radiocarbon determinations using accelerator mass spectrometry. Herein, it will be demonstrated how this can be achieved by a careful choice of method parameters and, most importantly, by the identification, quantification, and suppression of all sources of contamination associated with the PCGC isolation of single compounds. The main practical aspects of PCGC considered in this chapter are:

(i) Optimisation of the C sample size and length of the PCGC trapping sequence.

(ii) The validity of the method used for correction for the methyl group added during the derivatization of FAs.

(iii) Identification and quantification of degradation products of the GC column stationary phase used in the PCGC instrument within realistic trapping windows.

(iv) Introduction of a new trap design to allow solventless recovery of isolated compounds.

(v) Implementation of a method for cleaning the PCGC to prevent cross-contamination, especially in the switching valve-trap transfer capillaries.

3.3 Procedure parameters and corrections

3.3.1 Choice of sample size

A study was performed to determine the minimum sample size required to obtain precise (below 30 years error) radiocarbon dates from analytes graphitised in the AGE 3 graphitisation system. Graphite samples were prepared with 5 samples sizes 100, 200, 500, 1000 μg of the reference $C_{18:0}$ FAME (directly dated; Section 2.3.3.1), together with the AMS standards that would be graphitised in the EA-AGE system alongside FAs extracted from pots (Sections 2.2.1,

2.4.8, 2.4.9; phthalic anhydride, Ox II, IAEA C7 and IAEA C8 standards; Table 3-1; Table 3-2; Figure 3-2; Appendix 1). This allowed evaluation of when measurement uncertainty became unacceptable for obtaining radiocarbon determinations precision below 30 years.

Table 3-1: Fraction modern and radiocarbon ages together with analytical uncertainties for the AMS analyses of varying amounts of the standard $C_{18:0}$ FAME (> 98%, Sigma Aldrich).

Sample details	BRAMS #	Mass (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)
$C_{18:0}$ - 0.1 mg-1	1046.1.1	105	1.0363 ± 0.0042	-287 ± 32
$C_{18:0}$ - 0.1 mg-2	1046.1.2	128	1.0370 ± 0.0040	-292 ± 32
$C_{18:0}$ - 0.2 mg-1	1046.1.3	218	1.0331 ± 0.0035	-262 ± 28
$C_{18:0}$ - 0.2 mg-2	1046.1.4	207	1.0351 ± 0.0035	-277 ± 28
$C_{18:0}$ - 0.5 mg-1	1046.1.5	501	1.0291 ± 0.0031	-231 ± 25
$C_{18:0}$ - 0.5 mg-2	1046.1.6	524	1.0334 ± 0.0031	-264 ± 25
$C_{18:0}$ - 1.0 mg-1	1046.1.7	994	1.0347 ± 0.0031	-274 ± 25
$C_{18:0}$ - 1.0 mg-2	1046.1.8	994	1.0320 ± 0.0031	-253 ± 25

Table 3-2: Fraction modern and radiocarbon age with analytical uncertainties for the AMS analyses of varying amounts phthalic anhydride standard (Sigma Aldrich) used as blank material.

Sample details	BRAMS #	Mass (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)
Phthalic anhydride - 0.1 mg-1	1029.1.16	104	0.0112 ± 0.0253	36,090 ± 203
Phthalic anhydride - 0.1 mg-2	1029.1.17	114	0.0107 ± 0.0262	36,458 ± 211
Phthalic anhydride - 0.2 mg-1	1029.1.18	209	0.0064 ± 0.0233	40,627 ± 187
Phthalic anhydride - 0.2 mg-2	1029.1.19	227	0.0056 ± 0.0242	41,617 ± 195
Phthalic anhydride - 0.5 mg-1	1029.1.20	543	0.0043 ± 0.0210	43,842 ± 168
Phthalic anhydride - 0.5 mg-2	1029.1.21	559	0.0039 ± 0.0226	44,471 ± 181
Phthalic anhydride - 1.0 mg-1	1029.1.22	997	0.0021 ± 0.0385	49,697 ± 310
Phthalic anhydride - 1.0 mg-2	1029.1.23	983	0.0019 ± 0.0410	50,444 ± 330

The fraction modern ($F^{14}C$) obtained for the different amounts of $C_{18:0}$ FA measured were all identical within a 2σ error and averaged to 1.0338 ± 0.0012 (T' = 3.8, T'(5%) = 14.1, υ = 7) supporting the hypothesis that the amount of C has no significant effect on the accuracy of the AMS measurements. The analytical uncertainty associated with the measurement however increases (i.e. decrease in precision) with smaller sample sizes, i.e. with less C present. It is noteworthy that, for 500 µg, the error, 0.0031, is the same as for full-size. The error for 200 µg is 0.0035 against 0.0040 and 0.0042 for the 100 µg size.

With decreasing amounts of C, the blanks (i.e. background) increase from ~50,000 BP (1 mg of C) to ~36,000 BP (100 µg of C). Therefore, there is a size dependant background and small

C sizes could be an issue with 'old' archaeological materials which age is close to the limit of detection of ^{14}C. In such cases, the ^{14}C measurements of the phthalic anhydride are higher than a pure infinite age material and could affect the accuracy of the ^{14}C measurements when used for correction of the background contamination during the sample preparation.

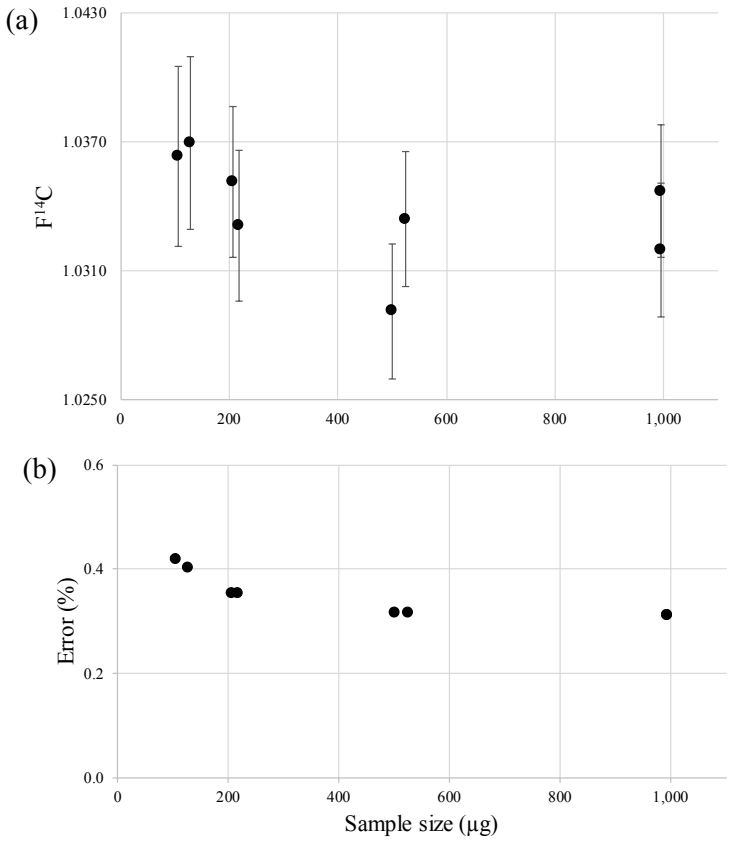

Figure 3-2: (a) $F^{14}C$ and (b) analytical error (in %) of the $C_{18:0}$ FAME plotted against sample size (µg).

These data from the FAs date suggest that a minimum of 200 µg of C should be used with the graphitisation system for obtaining the precision required. This would allow for a 'reasonable' error associated to the ^{14}C measurements (i.e. high precision) and limit the destruction of the pottery vessels for the extraction of 200 µg of C instead of 1 mg (commonly used). With this size the background obtain from the graphitisation and AMS procedure is ~40,000 so not too high for the application on lipids extracted from pottery vessels (the oldest pottery vessels known are ca. 20,000 BP; Wu *et al.* 2012) and CSRA dated. Therefore, in the rest of this thesis

200 µg of C are isolated by PCGC. Size-dependent effects of contamination were addressed previously in the literature (e.g. Santos *et al.* 2007; Santos *et al.* 2010) and are not the scope of the rest of this Chapter.

3.3.2 Column, GC program and trapping sequence parameters

In order to significantly shorten protocol required to isolate ca. 200 µg C with PCGC for AMS analysis in as shorter time as possible two modifications were made: (i) the stationary phase thickness was increased from 0.5 to 1.5 µm, allowing the injection of more concentrated lipid extracts (~ 5 $\mu g.\mu L^{-1}$), and (ii) the GC temperature program was shortened to 23 min (Section 2.4.7; Table 3-3); examples of gas chromatograms obtained are given in Figure 3-3.

Table 3-3: Comparison of the GC parameters used by Stott *et al.* (2003) and in this thesis.

Parameters	Stott method (2003)	New method
Stationary phase	DB-1	DB-1
Column length	30 m	30 m
Phase thickness	0.5 µm	1.5 µm
Sample concentration	~1-1.5 µg/µL	~ 5 µg/µL
GC run time	45 min	23 min
Number of injections	120	40
Trapping sequence length	5 days	20 hours

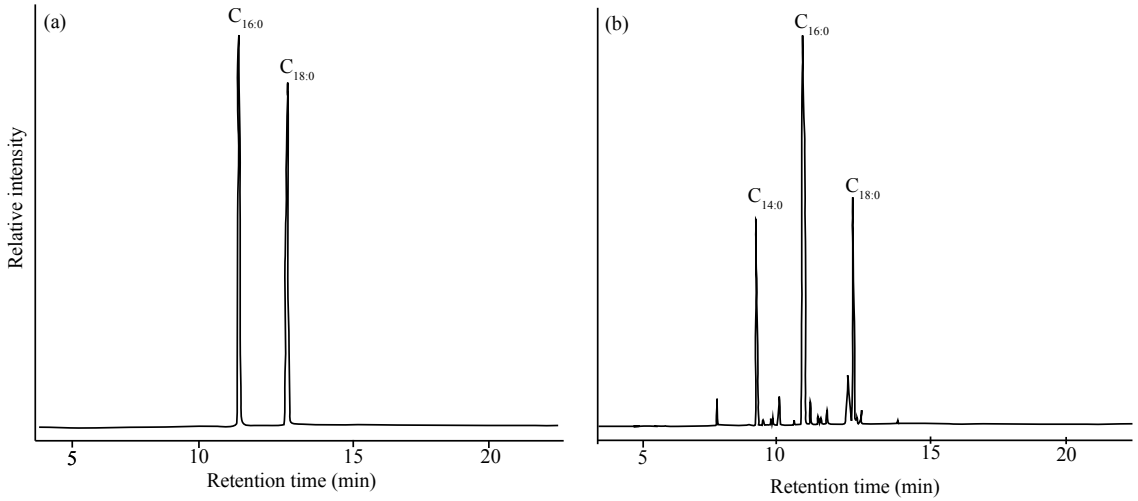

Figure 3-3: Partial gas chromatograms of: (a) standard FAME solution, and (b) an archaeological bog butter showing the $C_{16:0}$ and $C_{18:0}$ FAMEs characteristic of animal fats, using the PCGC temperature program shortened to 23 min.

These changes allow the isolation of 200 μg of C from FAMEs in only 20 hours. This means that one lipid extract per day, or five per working week, can be prepared, in contrast to a single lipid extract a week achieved previously. This was a critical step in making the method routine.

3.3.3 Correction of FAMEs for derivatising methyl group

The FAs are derivatised during their extraction into fatty acid methyl esters (FAMEs, Section 2.3.4.1), making them amenable for isolation using a non-polar GC column. The derivatisation adds an extra C per molecule that will affecting the measured radiocarbon date and thus requires correction. Two types of correction can be applied: (i) a simple mass balance ratio (Equation 2-8, referred as $F^{14}C_{FA.1}$), or (ii) a more refined correction, which considers the fractionation occurring during the methylation process (Equation 2-9, referred as $F^{14}C_{FA.2}$).

To evaluate the efficiency of such a correction, two modern fatty acids were purchased (Section 2.2.1) then dated before and after methylation (no PCGC isolation). The direct measurements on the fatty acid (Table 3-4, Figure 3-4) passed the χ^2 test at the 5 % level and the weighted average is $F^{14}C_{FA}$ = 1.0430 ± 0.15 (T' = 1.5, T'(5 %) = 9.5, υ = 4) for the $C_{16:0}$ FA and $F^{14}C_{FA}$ = 1.0537 ± 0.15 (T' = 0.3, T'(5 %) = 9.5, υ = 4) for the $C_{18:0}$ FA, thus this serve as the accepted $F^{14}C$ values on the FAs.

The measurements on the methylated FA passed the χ^2 test at the 5 % level for the $C_{16:0}$ (T' = 7.6, T'(5 %) = 9.5, υ = 4) and the $C_{18:0}$ (T' = 4.6, T'(5 %) = 9.5, υ = 4). This demonstrates a good level of scatter and precision for the methylation process. It is noteworthy that the errors recorded on the methylated FAs resulted in higher analytical uncertainty than the direct measurements made on the FAs. When applying the mass balance ratio correction then $F^{14}C_{FA.1}$ = 1.0435 ± 0.20 for the $C_{16:0}$ and $F^{14}C_{FA.1}$ = 1.0528 ± 0.20 for the $C_{18:0}$. These values are all identical within error to the weighted average of direct measurements (excepting

BRAMS-1086.2.1 which is just outside the 2σ range) demonstrating the accuracy of the radiocarbon determinations after correction.

When applying the second correction for fractionation then $F^{14}C_{FA.2}$ = 1.0428 ± 0.20 for the $C_{16:0}$ and $F^{14}C_{FA.2}$ = 1.0521 ± 0.20 for the $C_{18:0}$. These values are identical within error to the weighted average of the direct measurements, demonstrating the accuracy of the radiocarbon determinations after correction.

A difference was observed of 0.5 ‰ from the weighted average value of $F^{14}C_{FA}$ and $F^{14}C_{FA.1}$, and of 0.2 ‰ from the average value of $F^{14}C_{FA}$ and $F^{14}C_{FA.2}$ for the $C_{16:0}$ FA. The difference between the two corrections is 0.7 ‰ (i.e. 5-6 y). For the $C_{18:0}$ FA the difference of the average values of $F^{14}C_{FA}$ and $F^{14}C_{FA.1}$ is 0.9 ‰ and that between $F^{14}C_{FA}$ and $F^{14}C_{FA.2}$ is 1.6 ‰. The difference between the two corrections is also 0.7 ‰. There is, therefore, a constant shift of 5 years between the two corrections, this difference is negligible as it falls in the range of the typical error measurement of an AMS analysis.

Both corrections met the accuracy expected after correction as the results are statistically indistinguishable from the direct measurements. These results show the validity of both correction methods within the error measurement of an AMS. One factor of note in determining $F^{14}C_{FA.2}$ is that it requires measuring the stable C isotope value of the FA using another instrument (GC-C-IRMS), which increases both the time and cost of a radiocarbon determination. Therefore, as a simple mass balance ($F^{14}C_{FA.1}$) is sufficient to obtain an accurate correction for the methyl group added during the extraction of lipids, this mass balance approach will be used in the remainder of this thesis.

Table 3-4: Fraction modern of $C_{16:0}$ and $C_{18:0}$ FA directly dated before and after methylation. $F^{14}C_{FA}$ corresponds to the fatty acid, $F^{14}C_{FAME}$ correspond to the fatty acid after methylation, $F^{14}C_{FA.1}$ to the correction of additional Me group using a mass balance, and $F^{14}C_{FA.2}$ to the correction using the refined correction to account for fractionation. The sigma range is compared to the average of the direct measurements.

Sample	Direct measurement			Measurement after methylation					
	BRAMS #	**$F^{14}C_{FA} \pm 1\sigma$**	**σ range**	**BRAMS #**	**$F^{14}C_{FAME} \pm 1\sigma$**	**$F^{14}C_{FA.1} \pm 1\sigma$**	**σ range**	**$F^{14}C_{FA.2} \pm 1\sigma$**	**σ range**
$C_{16:0}$ FA	1086.1.1	1.0458 ± 0.0035	*	1086.2.1	0.9715 ± 0.0046	1.0322 ± 0.0046	**X**	1.0315 ± 0.0046	**X**
	1086.1.2	1.0418 ± 0.0034	*	1086.2.2	0.9847 ± 0.0045	1.0462 ± 0.0045	*	1.0455 ± 0.0045	*
	1086.1.3	1.0423 ± 0.0034	*	1086.2.3	0.9845 ± 0.0045	1.0461 ± 0.0045	*	1.0454 ± 0.0045	*
	1086.1.4	1.0406 ± 0.0034	*	1086.2.4	0.9858 ± 0.0045	1.0475 ± 0.0045	*	1.0467 ± 0.0045	*
	1086.1.5	1.0445 ± 0.0034	*	1086.2.5	0.9837 ± 0.0045	1.0451 ± 0.0045	*	1.0444 ± 0.0045	*
	Weighted average	**1.0430 ± 0.0015**		**Weighted average**	**0.9847 ± 0.0022**	**1.0435 ± 0.0020**	*	**1.0428 ± 0.0020**	*
$C_{18:0}$ FA	1085.1.1	1.0527 ± 0.0035	*	1085.2.1	1.0018 ± 0.0045	1.0575 ± 0.0045	*	1.0568 ± 0.0045	*
	1085.1.2	1.0545 ± 0.0035	**	1085.2.2	0.9914 ± 0.0046	1.0464 ± 0.0046	**	1.0458 ± 0.0046	**
	1085.1.3	1.0526 ± 0.0035	*	1085.2.3	0.9974 ± 0.0044	1.0529 ± 0.0044	*	1.0522 ± 0.0044	*
	1085.1.4	1.0545 ± 0.0035	*	1085.2.4	1.0016 ± 0.0045	1.0573 ± 0.0045	*	1.0566 ± 0.0045	*
	1085.1.5	1.0540 ± 0.0035	*	1085.2.5	0.9946 ± 0.0045	1.0499 ± 0.0045	*	1.0492 ± 0.0045	**
	Weighted average	**1.0537 ± 0.0015**		**Weighted average**	**0.9974 ± 0.0022**	**1.0528 ± 0.0022**	*	**1.0521 ± 0.0022**	*

* identical within a 1σ range of the weighted average of the direct measurement
** identical within a 2σ range of the weighted average of the direct measurement
X not identical within a 1 or 2σ to the weighted average of the direct measurement

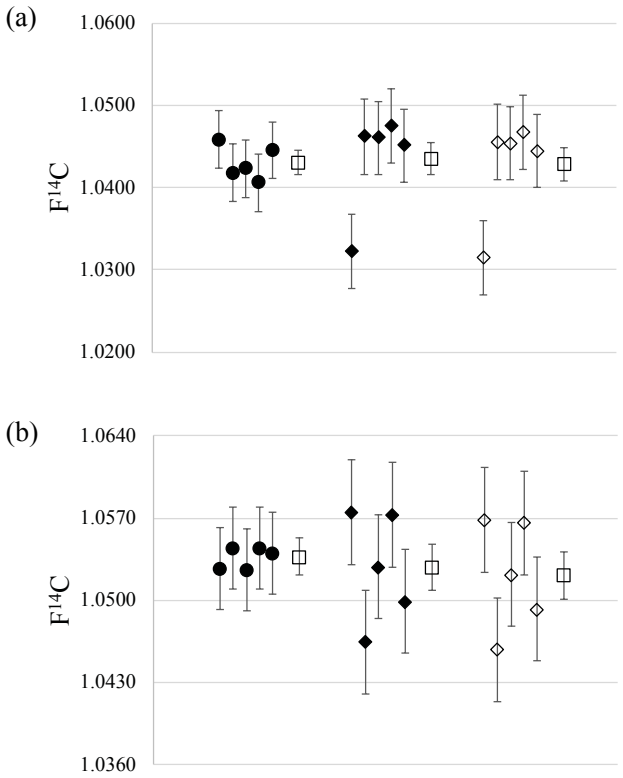

Figure 3-4: $F^{14}C$ of the (a) $C_{16:0}$ and (b) $C_{18:0}$ fatty acids. Black dots are $F^{14}C_{FA}$, black diamonds $F^{14}C_{FA.1}$ and white diamonds $F^{14}C_{FA.2}$. The errors shown are the measurement errors. White squares are the weighted average with weighted error.

3.4 Identification and quantification of exogenous C from the PCGC

In order to directly quantify exogenous C introduced by the PCGC instrument a standard solution of $C_{16:0}$ and $C_{18:0}$ FAME was isolated through the PCGC instrument and the content of the traps (ca. 200 µg of C) analysed by NMR (Sections 2.3.3, 2.4.4 and 2.5.2).

3.4.1 NMR analysis for the identification and quantification of bleed products

3.4.1.1 Identification of bleed products by NMR and GC/Q-ToFMS

NMR was used to assed exogenous C isolated by PCGC. All reference compounds (FAMEs, PDMS) were analysed individually by ^1H NMR to assess their chemical shifts (Figure 3-5). The reference FAMEs (methyl stearate and methyl palmitate), $CH_3(A)-COO-CH_2(B)-CH_2(C)$

$-(CH_2)_{12\ (or\ 14)}$(D)$-CH_3$(E), present a singlet at 3.69 ppm (A), a triplet centred on 2.32 ppm (B), a pentet at 1.64 ppm (C), a range of peaks at 1.35−1.20 ppm (D), and a triplet centred on 0.9 ppm (E). The reference cyclic poly(dimethylsiloxanes) present peaks at 0.20 ppm, for the hexamethylcyclotrisiloxane (*n* = 3-; *n* being the number of cyclic oligomer of the monomer unit -[$Si(CH_3)_2$-O]$_n$-; Section 3.1.2), 0.12 ppm for the octamethylcyclotetrasiloxane (*n* = 4-) and 0.10 ppm for the decamethylcyclopentasiloxane (*n* = 5-).

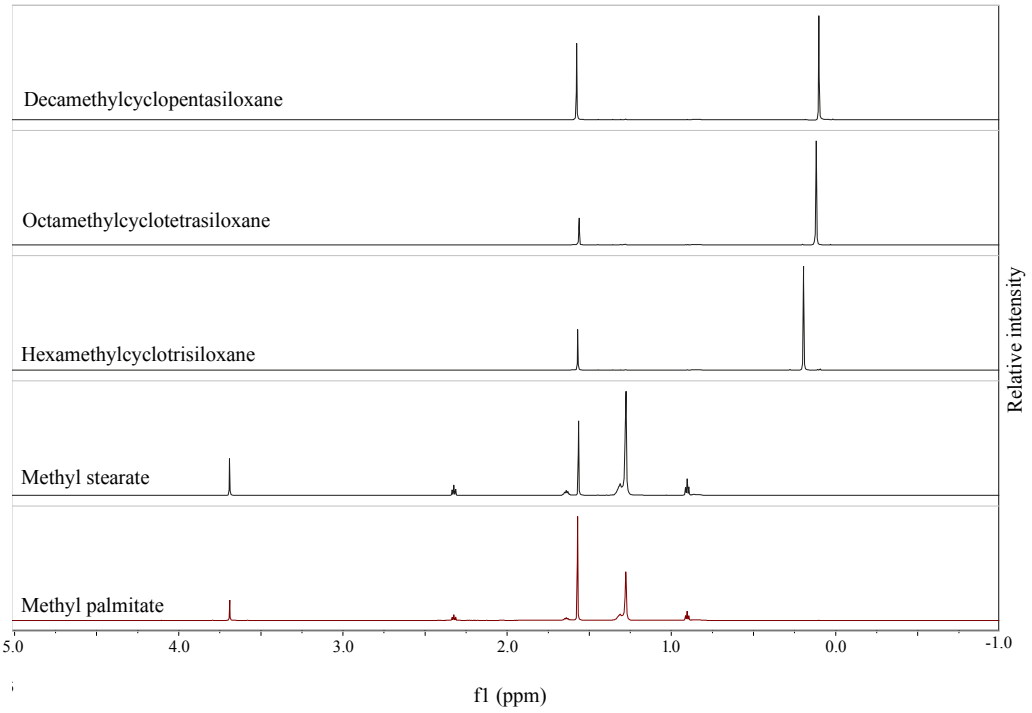

Figure 3-5: ^{1}H NMR spectra of reference FAMEs and stationary phase degradation products.

The NMR spectra of isolated compounds contained resonances at chemical shifts which corresponded to the reference $C_{16:0}$ or $C_{18:0}$ FAMEs (3.69 ppm, 2.32 ppm, 1.64 ppm, 1.35 - 1.20 ppm, and 0.9 ppm; Figure 3-6). In spectra displayed at full scale, i.e. normalised to the FAME 1.31 ppm peak, the resonances of the FAME are evident. However, unlike the reference compounds and blanks, close inspection of the baseline revealed that in all of the FAMEs isolated by PCGC peaks were clearly visible at 0.09 and 0.11 ppm with relative intensities lower than 0.06%; these are exogenous C derived from the PCGC instrument.

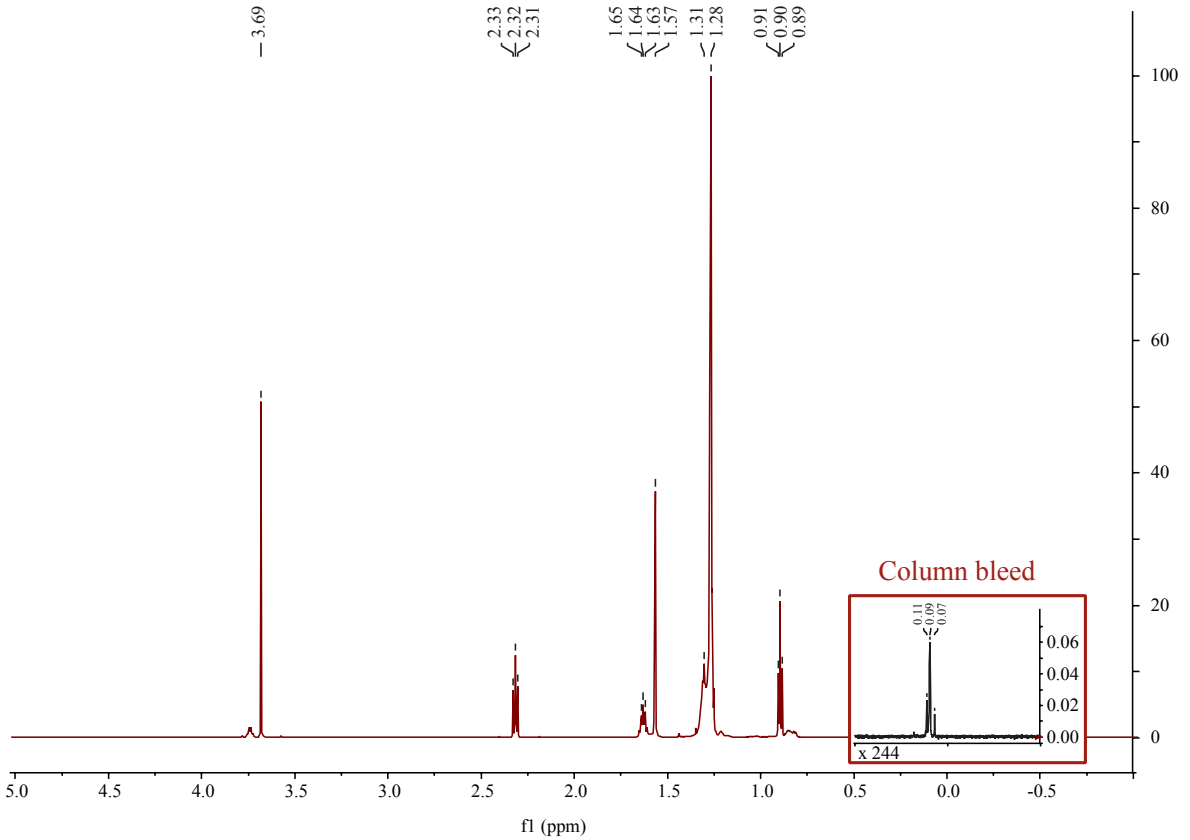

Figure 3-6: Normalised ^{1}H NMR spectrum of sample 2-$TC_{18:0}$ with magnification of the column bleed resonances at 0.07, 0.09 and 0.11 ppm.

The chemical shift values of 0.09 and 0.11 ppm indicate that the exogenous compounds trapped are likely a mixture of octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane derived from column bleed. The ^{1}H NMR spectra of some of the trapped compounds also contained a weaker peak at δ 0.07 ppm likely corresponding to a cyclic poly(dimethylsiloxanes) with an $n > 6$ membered ring. However, this identification, which is only based on chemical shifts, is limited. It should be noted that while other very minor peaks of similar intensity to the cyclic poly(dimethyl siloxane) were present in the ^{1}H NMR spectra, they also occur in the reference compounds and/or blank spectra. Therefore, these components can be eliminated as deriving from the PCGC, confirming that column bleed is the only source of exogenous C detectable from the trapping process.

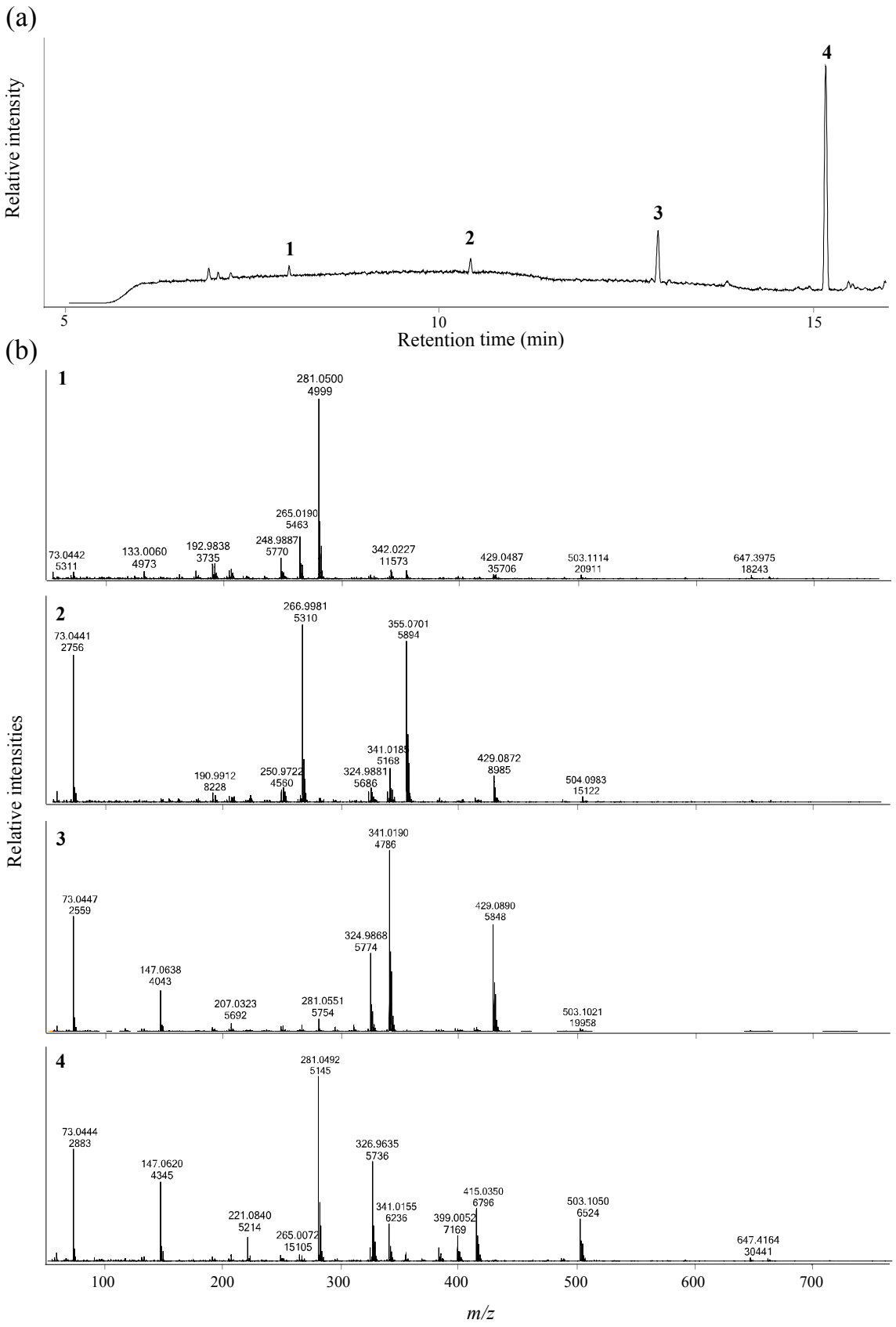

Figure 3-7: (a) Partial gas chromatogram of a sample isolated via PCGC showing PDMS degradation products (peaks 1-4). (b) Mass spectrum of the peaks (1-4) identified respectively, by comparison to reference standards, to the PDMS products with n = 4, 5, 6 and 7 moieties.

GC/Q-TOFMS (Section 2.4.5) was used to further investigate the nature of the column bleed. The TIC shown in Figure 3-7 revealed different proportions of oligomers *n* = 4-, 5-, 6- and 7- were confirmed by their individual mass spectra compared to the one of the reference compounds. The *n* = 3- oligomer was undetectable in all the trapped FAMEs. It is possible that cyclic oligomers *n* > 7- degradation products are present with the analytes but could not be identified due to a short elution window up to 16 min was analysed to avoid saturation of the mass spectrometer with FAMEs and IS. In line with the NMR results, the only impurities found to have been isolated with the FAs (other than those visible in the blank) and visible with the window chosen for the GC/Q-TOFMS are cyclic PDMSs.

3.4.1.2 Quantification of bleed components by NMR

The quantification of the amount of column bleed trapped with the FAMEs during PCGC was performed by establishing a calibration curve covering the concentration range 1 $mg.mL^{-1}$ to 1.10^{-6} $mg.mL^{-1}$ based on the peak areas of the methyl group protons (singlet at 3.69 ppm) of the $C_{18:0}$ FAME and those of the cyclic poly(dimethylsiloxane) methyl group protons (singlet at 0.20 ppm) for the hexamethylcyclotrisiloxane (Table 3-5). The signal for the lowest concentration of hexamethylcyclotrisiloxane was too weak for integration and therefore not included in the calibration. Plotting {peak area siloxane/peak area of FAME} against the ratio {mass of C siloxane/mass of C FAME}, produced a curve described by a linear regression with a slope of 25.843 ± 0.612. The correlation coefficient $R^2 = 0.999$, confirms a linear calibration curve has been obtained, which could be used for the required quantitative analyses.

GC/FID analysis of the trap contents demonstrated that the FAMEs isolated by PCGC contained only one FAME, i.e. no $C_{18:0}$ was detected in the trap intended to trap $C_{16:0}$ and *vice versa*. The C content of the isolated FAMEs varied from 112 µg to 264 µg of C (Table 3-6).

The variation in analyte recovery from the traps could have a number of causes; the most likely being the gradually increasing concentration of the standard solution in the autosampler vial due to solvent evaporation from the lipid extracts the sequence, or the loss of analyte during solvent evaporation under a stream of N_2. Overall, the average of sample recovery was 202 µg of C which was very close to the targeted trapping amount.

Table 3-5: Concentration, mass of C in the FAMEs and siloxanes and peak areas of the standards in the solutions prepared for the calibration curve. The NMR peak area of the FAME was the CH_3 group (3.6 ppm), the siloxane was hexamethylcyclotrisiloxane (0.20 ppm).

[FAME] ($mg.mL^{-1}$)	[Siloxane] ($mg.mL^{-1}$)	Area FAME	Area siloxane	$A_{Siloxane}$ / A_{FAME}	mC_{FAME} (mg)	$mC_{siloxane}$ (mg)	$mC_{siloxane}$ / mC_{FAME}
1	1.00E+00	1.12	12.23	1.09E+01	3.82E-02	1.62E-02	4.24E-01
1	1.00E-01	0.15	0.21	1.40E+00	3.82E-02	1.62E-03	4.24E-02
1	1.00E-02	0.15	0.02	1.33E-01	3.82E-02	1.62E-04	4.24E-03
1	1.00E-03	4.01	0.05	1.25E-02	3.82E-02	1.62E-05	4.24E-04
1	1.00E-04	3.97	0.01	2.52E-03	3.82E-02	1.62E-06	4.24E-05
1	1.00E-05	1.06	0	0	3.82E-02	1.62E-07	4.24E-06

Table 3-6: Details of FAMEs trapped by PCGC, associated column bleed in trapped compounds and calculated shifts towards older values in years. The trap $TC_{16:0}$ and $TC_{18:0}$ contained the $C_{16:0}$ and $C_{18:0}$ FAMEs, respectively.

Sample		$A_{Siloxane}$ /A_{FAME}	m_{FAME} trapped (µg)	mC_{FAME} (µg)	$mC_{siloxane}$ (ng)	$mC_{Siloxane}$ / mC_{FAME}	ΔAge (y)
Replicate	**Trap**						
1	**U-$TC_{16:0}$**	3.02E-03	286	205	24	1.17E-04	1
	G-$TC_{18:0}$	1.41E-03	232	177	10	5.46E-05	1
2	**G-$TC_{16:0}$**	7.09E-04	242	173	5	2.74E-05	0
	G-$TC_{18:0}$	5.01E-03	276	211	41	1.94E-04	2
3	**G-$TC_{16:0}$**	7.73E-03	322	231	69	2.99E-04	2
	G-$TC_{18:0}$	8.29E-03	184	141	45	3.21E-04	3
4	**G-$TC_{16:0}$**	8.32E-04	378	271	9	3.22E-05	0
	G-$TC_{18:0}$	5.09E-03	345	264	52	1.97E-04	2
5	**G-$TC_{16:0}$**	3.40E-03	157	112	15	1.32E-04	1
	G-$TC_{18:0}$	1.39E-03	307	234	13	5.37E-05	0
Average		**3.69E-03**	**273**	**202**	**28**	**1.43E-04**	**1**

Based on the mass of C trapped, the NMR peak areas and the calibration curve slope, the amount of C from the column bleed was determined (Equation 2-4; Table 3-6). The C contributing from column bleed in the trapped FAMEs ranged from 5 ng (sample 2 - $TC_{16:0}$) to 69 ng (sample 3 – $TC_{16:0}$), with a mean of 28 ng. It is noteworthy that no significant difference was observed in the amount of column bleed detected in the traps $TC_{16:0}$ and $TC_{18:0}$. This

confirms that, for these trapping windows, under these conditions, the temperature of the GC oven had no appreciable effect on the amount of column bleed eluting from the GC column.

The amount of infinite age C from column bleed introduced into the amount trapped FAMEs correspond to 0.03 ‰ to 0.32 ‰ contamination, with a mean of 0.14 ‰; this is well below the critical theoretical limit of 1 ‰ radiocarbon dead contamination that would significantly affect high precision radiocarbon dates (Figure 3-8). The level of contamination observed is equivalent to a shift of 0 to 3 years towards older dates, which is well within the maximum precision achievable by AMS. Therefore, column bleed will not have a significant effect on ^{14}C dates of compounds isolated by PCGC and, hence, its effect can be disregarded with regards to corrections of dates.

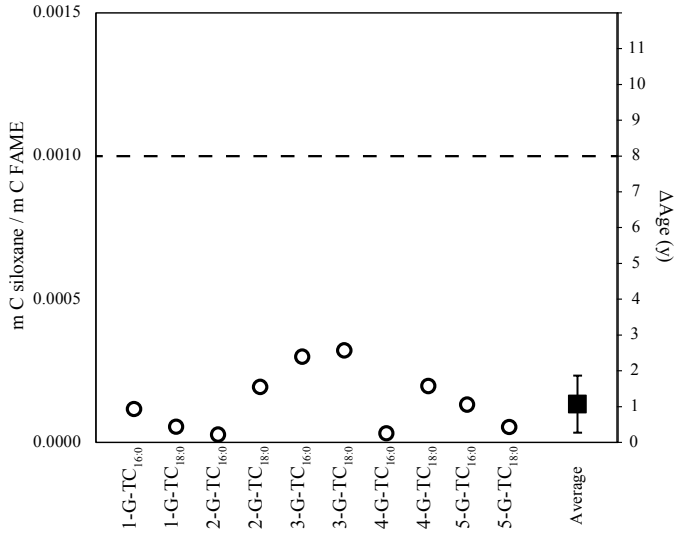

Figure 3-8: Ratio of the mass of C from PDMS to the mass of C from the trapped FAME, for all the samples investigated (dot). The square corresponds to the average and error bar shows the standard deviation. The dashed line corresponds to the threshold of column bleed contamination of 1 ‰ that would affect ^{14}C determinations by AMS.

3.4.2 Application to an archaeological pottery vessel

The NMR method was then applied to a lipid extract from an archaeological vessel (ROS-C-4678; Section 2.3.2.1) to verify that no other exogenous C would exist with

archaeological materials. The lipid concentration in the pottery vessel was 4.6 $mg.g^{-1}$ of sherd fabric, with $C_{16:0}$ and $C_{18:0}$ FAs dominating the extract (Figure 3-9; see Chapter 5 for details of ORA). The GC temperature program was modified slightly due to the presence of other compounds in the TLE eluting at a higher temperature than the FAMEs. The trapping windows were shortened (~30 sec) due to the presence of compounds eluting close to the target FAMEs, especially the presence of a $C_{18:1}$ FAME eluting immediately before the $C_{18:0}$ FAME.

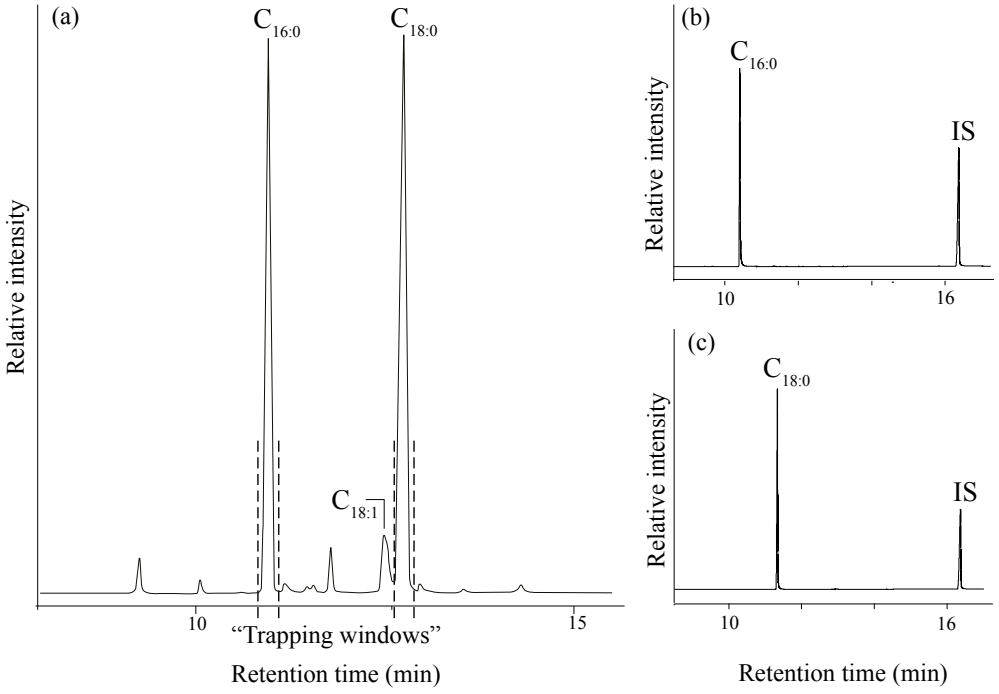

Figure 3-9: (a) Partial gas chromatogram of the invisible residues from the pottery vessel ROS-C-4695 with the dashed line corresponding to the trapping windows chosen; (b) and (c) partial gas chromatograms of the contents of the traps, respectively, Pot-$TC_{16:0}$ and Pot-$TC_{18:0}$ corresponding to the $C_{16:0}$ and $C_{18:0}$ trapping windows indicated in (a). IS is the internal standard added for quantification.

The results obtained with NMR analysis of the archaeological FAMEs are entirely analogous to those obtained from the standard FAMEs (Figure 3-10). The exogenous contamination was quantified to be 16 ng for the $TC_{16:0}$ and 15 ng for the $TC_{18:0}$ corresponding to a theoretical offset of 1 year towards older values for the amount of FAME trapped.

Low-intensity peaks other than the PDMS products were present in the NMR spectrum of $TC_{18:0.}$ The chemical shifts at 5.37, 4.13 and 1.98 ppm were signals associated with the $C_{18:1}$ isomers (confirmed by GC-MS analysis) of the $C_{18:0}$ FAME resulting from the chromatographic tail of the unsaturated components (Mottram *et al.* 1999). This contamination is, however, archaeological and contemporaneous with the $C_{18:0}$ FAME and not an exogenous contaminant.

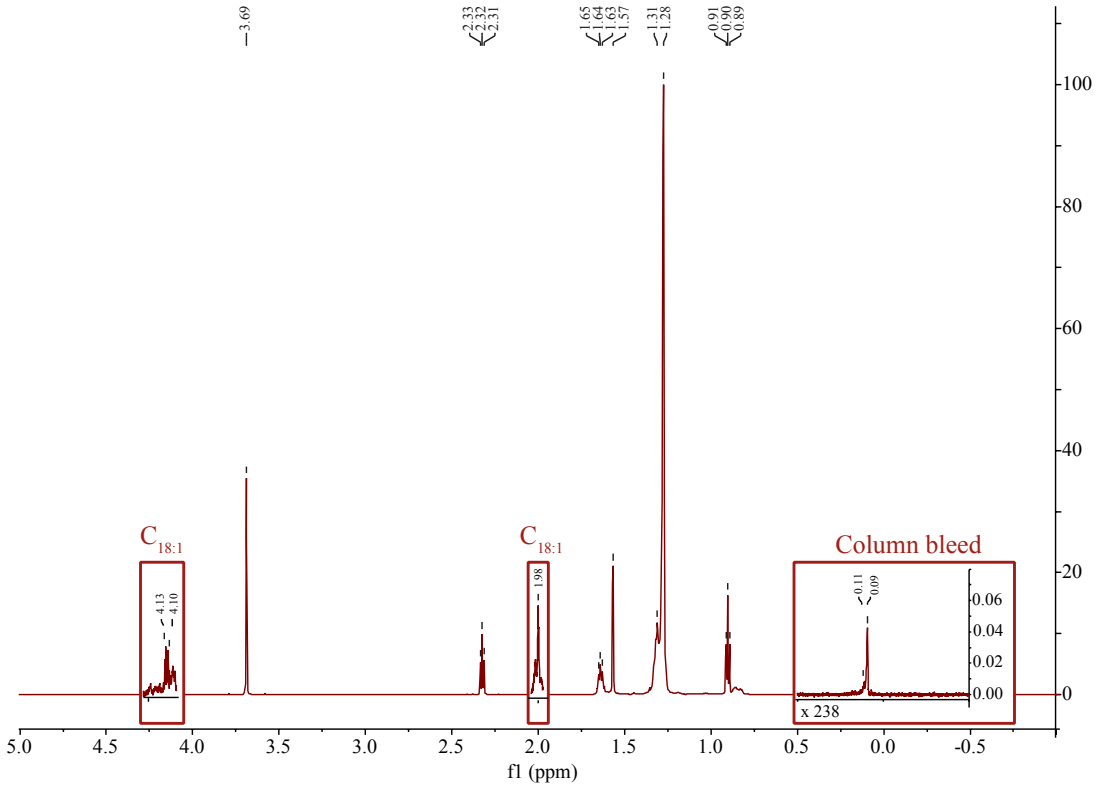

Figure 3-10: Normalised ^{1}H NMR spectra of sample Pot-$TC_{18:0}$ with magnification of the column bleed resonances at 0.09 and 0.11 ppm and unsaturated $C_{18:1}$ resonances at 1.98 and 4.13 ppm.

3.4.3 Discussion

The results represent the first direct identification and quantification of nanogram quantities of exogenous C in isolated analytes for radiocarbon dating by AMS. The results confirm that exogenous C is readily detectable by 700 MHz NMR at the ‰ concentrations that would affect high precision radiocarbon determinations by AMS. NMR spectra provide a comprehensive

overview of all the protonated chemical species present and, thus, is able to molecularly-identify other sources of extraneous C in trapped compounds, in addition to co-eluting column bleed. Finally, while the results presented demonstrate that the column bleed from the DB-1 column coated with a 1.5 µm thickness film is negligible, it is important to be aware that other phases, phase thickness or even deteriorating cross-linked poly(dimethyl siloxane) coated columns, or temperature programmes using higher temperatures, may produce sufficient bleed to have a significant effects on radiocarbon determinations. Thus, to guarantee the reliability of radiocarbon dates of compounds isolated by PCGC, determinations, such as those described here should be performed: (i) every time a new column is installed into a PCGC instrument, or (ii) when a compound with a different boiling point is isolated using a different temperature program. Processed standards would nonetheless be run with every batches for ^{14}C analyses.

3.5 A new trap design for a solventless recovery of isolated compounds

3.5.1 Influence of incomplete solvent removal by NMR

The Gerstel traps (G-Traps) or "U" tubes supplied with the preparative fraction collector consist of a coaxial tube with a side arm (Figure 3-11).

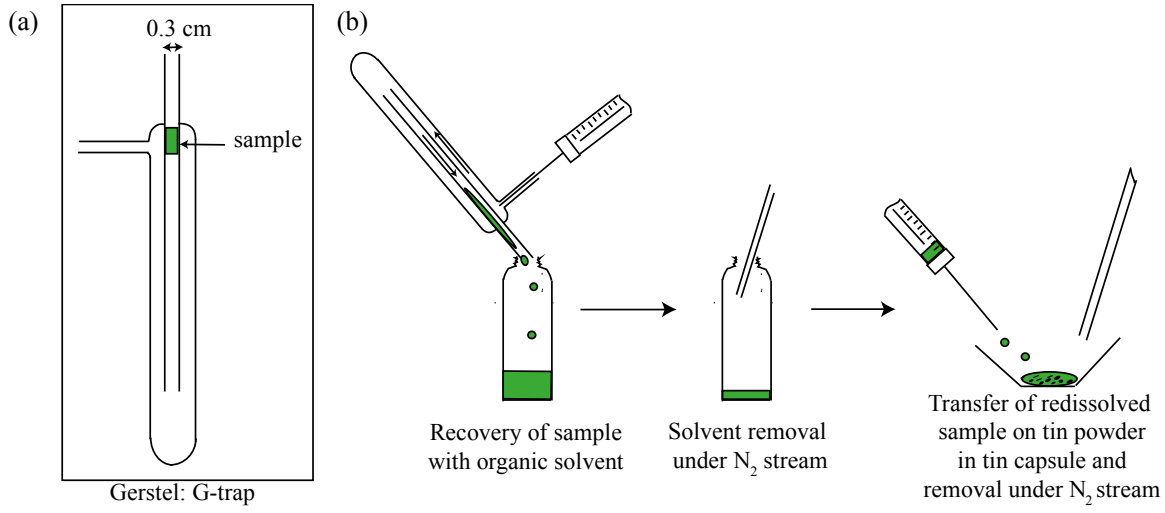

Figure 3-11: (a) Design of the Gerstel traps and (b) sample recovery method for the G-trap.

The column eluent flows down the interior channel, before flowing up the exterior and leaving the trap via a side-arm. The isolated compounds are generally condensed in the initial few mm of the trap and subsequently recovered by back-flushing the trap with an organic solvent followed and removal of the solvent from the resulting solution by blowing down under a gentle stream of N_2 (Stott *et al.* 2003). Therefore, some residual solvent used for recovery of samples has the potential to influence CSRA and need investigation (Eglinton *et al.* 1996).

After trapping, FAMEs from the standard solution (Sections 2.3.3, 2.4.7) were recovered from the G-Traps by rinsing with an organic solvent, such as DCM, then 'removing' the solvent under a stream of N_2. Despite the vials which contain the isolated compounds appearing solvent-free, the ^{1}H NMR spectra show a clear signal at 5.32 ppm corresponding to DCM protons (Figure 3-12).

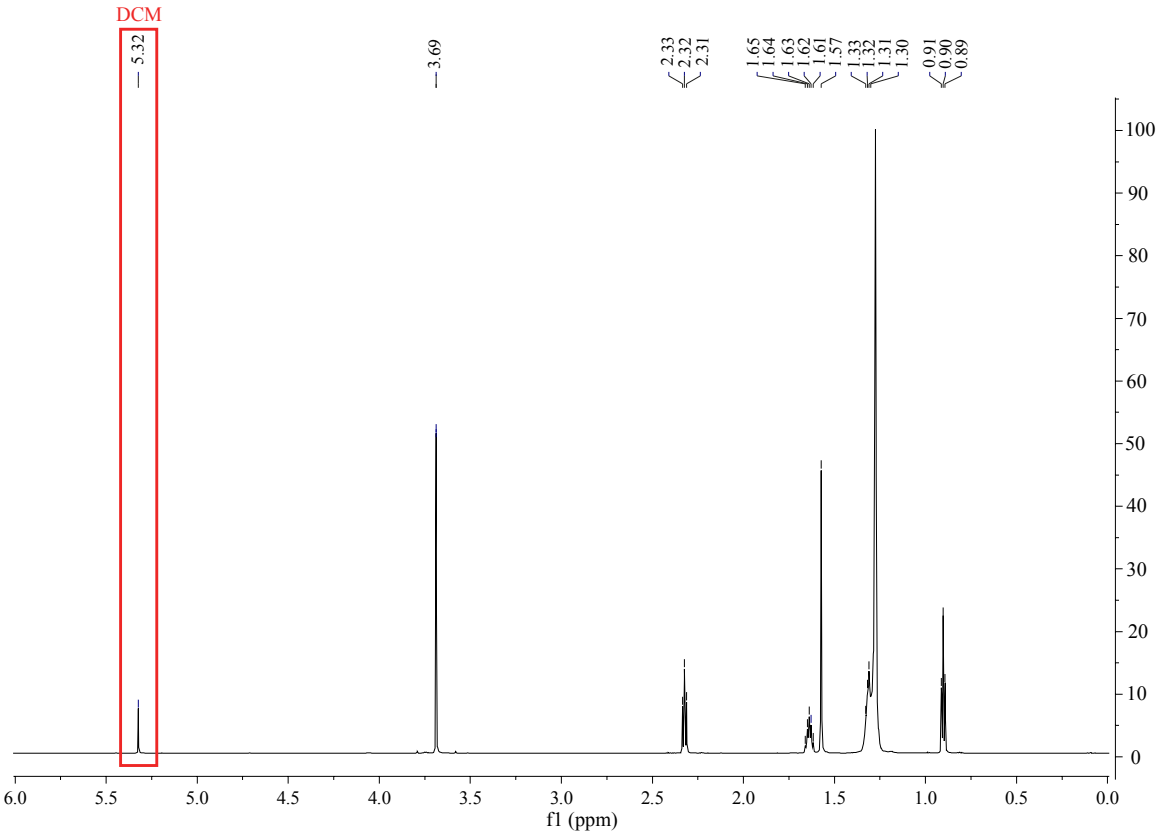

Figure 3-12: Partial ^{1}H NMR spectrum of $C_{16:0}$ isolated in G-Trap, recovered with DCM and blown down to dryness prior to NMR analysis. The resonances between 0.89 ppm and 3.69 ppm derived from the $C_{16:0}$ FAME and the resonance at 5.32 ppm corresponds to DCM.

The quantity of DCM present in the isolated FAMEs was calculated by comparison of the area of this peak with that of the methyl group on the FAMEs. The amount of C in the final analyte which is derived from the residual DCM as a proportion of the FAME C was found to be 7.4 ‰ (1.8 μg of C) contamination in trap $TC_{16:0}$ and 9.3 ‰ (2.1 μg of C) contamination in trap $TC_{18:0}$. Since DCM is a petroleum-derived product and thus contains no radiocarbon (i.e. it is radiocarbon 'dead'), this would equate to a shift in the determined radiocarbon dates of 60 and 75 years older than the true age, respectively. These offsets would be outside the 2σ (95 %) range required for high-precision radiocarbon determinations. These results clearly demonstrate the potential for problems resulting from the incomplete removal of solvent prior to radiocarbon dating, as originally recognized by Eglinton *et al.* (1996). The compounds trapped above were considered to be free of solvent before NMR analysis; although determining the presence of such solvent by GC is impossible. The amount of residual solvent variates between the samples, thus it is not a constant source of C that can be reliably corrected using standards. These results emphasize the need for a solventless system for the recovery of archaeological compounds isolated by PCGC for radiocarbon dating.

3.5.2 Evaluation of the performance of a new solventless trap design

3.5.2.1 Description of the solventless trap design

A new trap design was developed and tested (solventless trap or S-Trap, Figure 3-13) to replace the G-Traps. It consists of a borosilicate glass capillary (3 mm o.d, 1 mm i.d., 70 mm in length) containing a 10 mm glass wool plug positioned 15 mm from the top of the trap. The capillary tubes are connected to the PFC via PTFE ferrules in the same manner as the G-Traps. The analyte is condensed onto the glass wool, which can be physically removed from the trap by

pushing, with the tip of a pre-combusted glass Pasteur pipette, directly into a tin/foil capsule for combustion in an elemental analyser or into a glass tube for offline combustion.

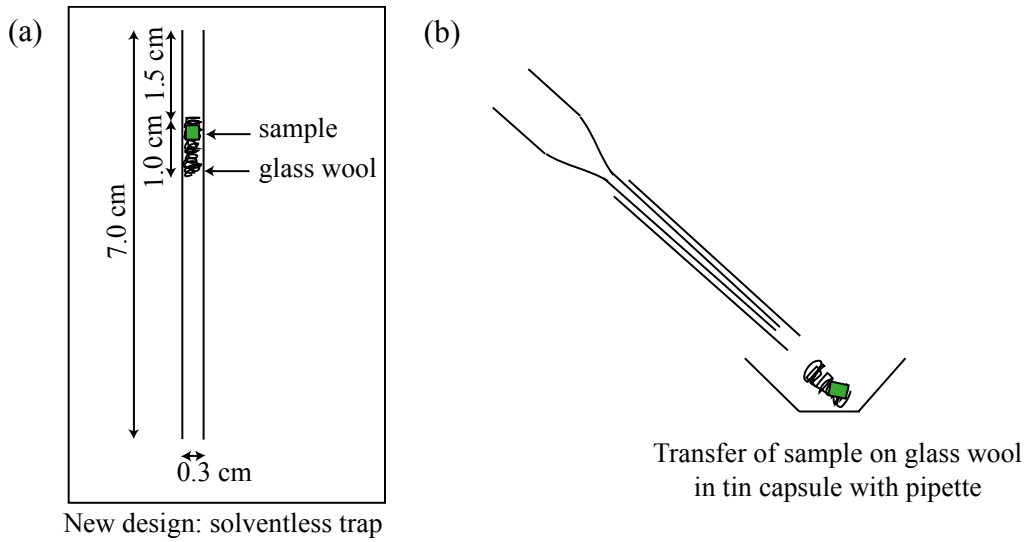

Figure 3-13: (a) New solventless trapping system. (b) Sample recovery method for the S-trap.

3.5.2.2 Determination of trapping efficiency

The FAMEs standard solution was isolated using both trap design for comparison (Sections 2.3.3, 2.4.7, 2.5.2). The percentages of C lost to waste (trap T_W), successfully trapped and recovered in both trap design are given in Table 3-7.

Table 3-7: Percentage of C recovered in the G-Trap and lost in the T_W; percentage of C trapped in the S-trap in the wool, lost on the side of the trap and in T_W (see Section 2.3.3.3).

Sample		**G-Trap**		**S-Trap**		
Replicate	**Trap**	**% C trapped**	**% C in T_W**	**% C trapped in glass wool**	**% C on side of the trap**	**% C in T_W**
1	**$TC_{16:0}$**	99.5	0.5	99.3	0.7	0.0
	$TC_{18:0}$	98.7	1.3	98.9	0.0	1.1
2	**$TC_{16:0}$**	99.0	1.0	95.4	4.6	0.0
	$TC_{18:0}$	99.1	0.9	88.6	9.6	2.0
3	**$TC_{16:0}$**	99.6	0.4	86.3	12.2	1.8
	$TC_{18:0}$	98.1	1.9	98.1	0.1	1.8
4	**$TC_{16:0}$**	99.9	0.1	95.8	3.8	0.4
	$TC_{18:0}$	99.0	1.0	97.7	0.1	2.1
5	**$TC_{16:0}$**	98.0	2.03	98.9	0.4	0.7
	$TC_{18:0}$	96.5	3.5	98.1	0.2	1.7
Average		**98.7**	**1.3**	**95.7**	**3.2**	**1.2**

The proportion of C from the FAME which was collected in the T_W was found to be 1.3 % in the case of the G-Traps, and 1.2 % in the case of the S-Traps. Any C transferred to the waste trap is likely to be a consequence of switching of the traps within the tail of the chromatographic peaks and should, therefore, be independent of the trap design; which is supported by the data as the amount of FAMEs lost in the waste is identical for both designs.

Using the S-Trap, a potential source of analyte loss would be due to condensation on the internal walls of the glass tube. Determination of the proportion of C lost on the sides of the tubes in the S-traps was shown to be 3.2 ± 4.4 % (1σ). While trapping losses up to 12.2 % were observed for the two highest losses in traps where the PFC capillary was not in contact with the glass wool. It can, therefore, be concluded that it is critical that the end of the capillary from the fraction collector is positioned to be in contact with the glass wool. Any dead-volume before the glass wool will promote turbulent flow and lead to analyte condensation on the walls of the tubes. However, the capillary termini must not be buried within the glass wool as this can cause a blockage and prevent the collection of the analyte. The average trapping efficiency of the glass wool in the S-traps is 95.7 % of the C introduced to the PCGC and the entirety of this C can be combusted directly for graphitization and radiocarbon analysis without any risk of evaporative loss during solvent removal or contamination with residual organic solvent.

3.5.2.3 Exogenous C associated with isolated compounds

As a full comparison to the G-Traps, column "bleed" associated with the isolated compounds in S-Trap has also been evaluated (Table 3-8 for S-traps data and Table 3-6 for G-Traps). The mean amount of contaminant C introduced during trapping into the S-Traps was found to be 4 ng or 0.03 ‰ contamination. This level of radiocarbon-dead contamination in the replicate samples would cause a shift in the determined radiocarbon date of <1 y to older values for the

amount of C trapped (Table 3-8). This is a lower level of contamination than was determined for compound trapped in the traditional G-Traps (0.14 ‰; ~1 y shift to older values).

Neither of the compounds recovered from the G-Traps or the S-Traps showed any detectable form of exogenous C other than poly(dimethyl siloxanes) by NMR analysis. The mean amount of column bleed isolated alongside the FAME standards was 28 ng C for the G-Traps and 4 ng C for the S-Traps. Neither represents a significant level of contamination, however, it is interesting that less column bleed was trapped using the new S-Trap design. This observed difference is unlikely to be due to differences in the condition of the GC column, as these trapping sequences were carried out 1 week apart on the same instrument with the same GC column installed. It could be that the internal walls of the S-Trap tube have a higher affinity for trapping poly(dimethyl siloxanes) than the glass wool or that being more volatile, the PDMSs are not retained on the glass wool, but the length of the G-Traps is sufficient to allow their condensation and recovery.

Table 3-8: Mass of C from the FAME and the column stationary phase degradation products, percentage of exogenous contamination and age shift associated with the S-Traps.

Sample		**S-Trap**			
Replicate	**Trap**	**mC_{FAME} (µg)**	**$mC_{Siloxane}$ (ng)**	**$mC_{Siloxane}$/ mC_{FAME} (‰)**	**ΔAge (y)**
1	**S-$TC_{16:0}$**	178	2	0.01	0
	S-$TC_{18:0}$	168	5	0.03	0
2	**S-$TC_{16:0}$**	127	0	0.00	0
	S-$TC_{18:0}$	148	3	0.02	0
3	**S-$TC_{16:0}$**	102	1	0.01	0
	S-$TC_{18:0}$	262	4	0.01	0
4	**S-$TC_{16:0}$**	167	7	0.04	0
	S-$TC_{18:0}$	141	5	0.03	0
5	**S-$TC_{16:0}$**	116	8	0.07	1
	S-$TC_{18:0}$	150	6	0.04	0
Average		**156**	**4**	**0.03**	**0**

3.5.2.4 Radiocarbon determinations, precision and accuracy

The scatter (measured as the standard deviation, SD) observed within radiocarbon determinations of replicate isolations and analyses of the same FAME standards was assessed

for both trap designs, giving a measure of the accuracy of the value obtained with each trap design (Table 3-9, Figure 3-4, Sections 2.3.3.3). It is clear from Figure 3-14 that the scatter (SD = 0.0088 and 0.0120 for the $C_{16:0}$ and $C_{18:0}$ FAMEs) observed in FAMEs isolated using the traditional G-traps with solvent recovery is far higher than the same FAMEs measured directly (SD = 0.0030 and 0.0021 for the $C_{16:0}$ and $C_{18:0}$ FAMEs). The FAMEs isolated using the new S-Trap design demonstrate a much lower degree of scatter (SD = 0.0041 and 0.0020 for the $C_{16:0}$ and $C_{18:0}$ FAMEs) of radiocarbon content and more closely reflect the values of the FAMEs determined without PCGC trapping.

Interestingly, the scatter observed in radiocarbon contents of FAMEs isolated from the G-Traps was not solely towards lower $F^{14}C$ values, as would be expected due to differing amounts of radiocarbon 'dead' C from residual solvent. Some replicates demonstrated significantly higher $F^{14}C$ values. The transfer of FAMEs in organic solvents from the G-Traps to tin capsules and the subsequent solvent removal under a stream of N_2 results in the analytes being exposed under the blow down for a prolonged period, and it is possible that additional ('modern') exogenous C could be introduced to analytes at this. The quick and simple transfer of the glass wool from the S-traps into tin capsules minimizes exposure to these sources of contamination.

The weighted means of the $F^{14}C$ values determined for the $C_{16:0}$ and $C_{18:0}$ FAME standards and their 1σ uncertainties were determined as 0.9882 ± 0.0015 and 1.0326 ± 0.0014, respectively. The weighted means for the $C_{16:0}$ and $C_{18:0}$ FAMEs from the G-traps were 0.9905 ± 0.0020 and 1.0253 ± 0.0020, respectively. Both sets of replicates failed the χ^2 test at the 5 % level (T' = 27.7, T'(5 %) = 9.5, υ = 4 and T' = 28.4, T'(5 %) = 9.5, υ = 4), indicating a far higher level of scatter than would be expected on a purely statistical basis.

Table 3-9: $F^{14}C$ values determined for FAME standards off-line and isolated by PCGC using the G- and S-traps.

Compound	Direct date			PCGC dates in G-Traps			PCGC dates in S-traps		
	BRAMS #	**$F^{14}C \pm 1\sigma$**	**σ range**	**BRAMS #**	**$F^{14}C \pm 1\sigma$**	**σ range**	**BRAMS #**	**$F^{14}C \pm 1\sigma$**	**σ range**
$C_{16:0}$ FAME	1047.1.1	0.9900 ± 0.0033	*	1048.3.1	0.9900 ± 0.0044	*	1048.8.1	0.9853 ± 0.0043	*
	1047.1.2	0.9905 ± 0.0033	*	1048.4.1	1.0009 ± 0.0045	X	1048.9.1	0.9843 ± 0.0043	*
	1047.1.3	0.9893 ± 0.0033	*	1048.5.1	0.9768 ± 0.0042	X	1048.10.1	0.9882 ± 0.0043	*
	1047.1.4	0.9883 ± 0.0033	*	1048.6.1	0.9929 ± 0.0044	*	1048.11.1	0.9810 ± 0.0043	**
	1047.1.5	0.9830 ± 0.0033	**	1048.7.1	0.9933 ± 0.0044	*	1048.12.1	0.9862 ± 0.0043	*
							1048.14.1	0.9873 ± 0.0037	*
							1048.16.1	0.9911 ± 0.0043	**
							1048.17.1	0.9942 ± 0.0044	**
	Weighted average	**0.9882 ± 0.0015**		**Weighted average**	**0.9904 ± 0.0020**		**Weighted average**	**0.9872 ± 0.0015**	
$C_{18:0}$ FAME	1046.1.3	1.0324 ± 0.0036	*	1048.3.2	1.0268 ± 0.0045	*	1048.8.2	1.0293 ± 0.0045	*
	1046.1.4	1.0341 ± 0.0036	*	1048.4.2	1.0164 ± 0.0045	X	1048.9.2	1.0296 ± 0.0045	*
	1046.1.5	1.0290 ± 0.0033	**	1048.5.2	1.0117 ± 0.0043	X	1048.11.2	1.0335 ± 0.0045	*
	1046.1.6	1.0335 ± 0.0033	*	1048.6.2	1.0413 ± 0.0047	X	1048.12.2	1.0271 ± 0.0045	*
	1046.1.10	1.0323 ± 0.0034	*	1048.7.2	1.0328 ± 0.0045	**	1048.14.2	1.0275 ± 0.0045	*
	1046.1.11	1.0347 ± 0.0034	*				1048.15.2	1.0304 ± 0.0040	*
							1048.16.2	1.0294 ± 0.0035	*
							1048.17.2	1.0310 ± 0.0034	*
	Weighted average	**1.0326 ± 0.0014**		**Weighted average**	**1.0253 ± 0.0020**		**Weighted average**	**1.0298 ± 0.0015**	

* measurement within 1σ range of the weighted average on direct dates for $C_{16:0}$ and $C_{18:0}$ FAMEs,
** measurement within 2σ range of the weighted average on direct dates for $C_{16:0}$ and $C_{18:0}$ FAMEs,
X measurement outside 2σ range of the weighted average on direct dates for $C_{16:0}$ and $C_{18:0}$ FAMEs

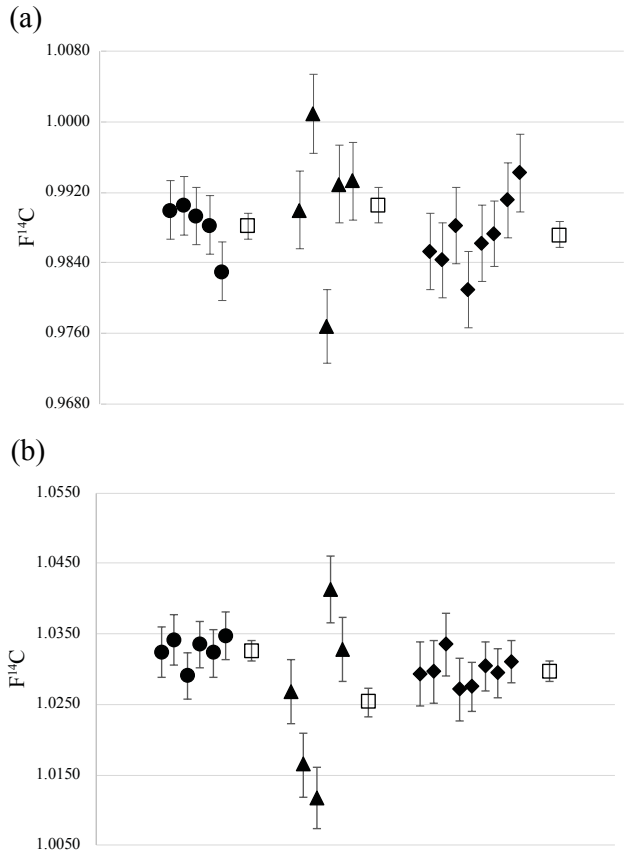

Figure 3-14: $F^{14}C$ values of (a) the $C_{16:0}$ and (b) $C_{18:0}$ FAME standards. Black dots represent off-line measurements, black triangles represent compounds isolated in the G-traps, black diamonds represent compounds isolated in the S-Traps and white squares to the weighted average. The error bars correspond the 1σ analytical uncertainty and weighted average respectively.

The replicates from both direct measurements of FAMEs and isolated in G-Trap were combined and again subjected to χ^2 tests and failed the 5 % level in the case of $C_{18:0}$ FAME (T' = 0.8, T'(5 %) = 3.8, υ = 1 and T' = 8.9, T'(5 %) = 3.8, υ = 1).

The weighted means for the $C_{16:0}$ and $C_{18:0}$ FAMEs from the S-Traps were 0.9872 ± 0.0015 and 1.0297 ± 0.0014, respectively. Both sets of replicates passed the χ^2 test at the 5 % level (T' = 6.2, T'(5 %) = 14.1, υ = 7 and T' = 1.5, T'(5 %) = 14.1, υ = 7), indicating acceptable levels of sample scatter (and therefore precision). The replicates from both direct and G-Trap analyses were combined and again subjected to χ^2 tests and passed at the 5 % level in each case (T' = 0.2, T'(5 %) = 3.8, υ = 1 and T' = 1.9, T'(5 %) = 3.8, υ = 1). This not only indicates that the precision of the S-trap method is excellent, but that the dates produced are accurate.

3.5.3 Summary

It is clear that the use of the new S-Trap design avoids the contamination of trapped analytes by residual solvent first raised by Eglinton *et al.* (1996) and confirmed unambiguously in this study by NMR and AMS analyses. The advantages of this new trapping approach include: (i) elimination of organic solvent for handling of isolated compounds, (ii) reduced GC column stationary phase column bleed, (iii) direct transfer of the single compounds from the trap to the tin/foil capsule for graphitization allowing fast recovery of single compounds from the traps, thereby minimizing the introduction of exogenous contaminants prior to graphitization, and (iv) reproducible and accurate ^{14}C determinations.

3.6 Cross contamination in the PCGC instrument

3.6.1 A new method of cleaning the trap capillaries to remove 'memory effect'

To facilitate the removal of cross-contamination in the instrument, all parts of the instrument require cleaning between successive trapping sequence. The syringe used for the injections must first be sonicated in solvent and the column, transfer line and capillaries should be heated to 300 ºC. The remaining possible problem area lies at the end of the capillaries which emanate from the PFC in the traps (that are at room temperature). There is, therefore, a 'cold spot' at the end of the capillary where analytes might condense either in or outside the capillaries, and thus can carried over into the new trap.

A simple cleaning method, established here, involved the use of a heat gun at 300 ºC under an elevated He flow to facilitate evaporation of residual condensed compounds from the end of the transfer capillaries connecting the switching valve to the traps.

3.6.2 Evaluation of effects of cross contamination/cleaning by GC analysis

Estimation of cross-contamination in the PFC was assessed by GC analysis of the contents of the clean trap installed immediately after a typical 40 run trapping sequence with a FAME standard ($C_{16:0}$ in T1 and $C_{18:0}$ in T2; Sections 2.5.2.3, 2.4.1). This was followed by injection of the standard FAMEs solution (Test 1 and 2; Table 3-10) and no compound was collected in the trap (T1) that contained $C_{16:0}$ in the previous injection and collecting the $C_{16:0}$ in the trap (T2) that contained $C_{18:0}$ in the previous injection. In the other Tests (3 to 9; Table 3-10) following the injection of the FAMEs standards pure solvent was injected and the eluent at similar retention times similar to the elution of the $C_{16:0}$ and $C_{18:0}$ standard was collected into the traps.

The results obtained by GC analysis (Test 1, 3-6) showed that residual FAMEs are carried over into the new traps, and the carryover is independent of the trap design (Figure 3-15a, c; Table 3-10). For Test 1, 61 µg of the residual $C_{18:0}$ FAME in T2 was trapped along the with the $C_{16:0}$ corresponding to ~1/5 of the total amount of analyte trapped, showing that a considerable amount of analyte from the previous trapping sequence remained in the switching valve and/or transfer capillary and is carried over into the next analyte trapped. With blank injections, the amount of FAME transferred into the clean traps ranged from 0.1 to 38 µg of C. The variation observed between residual $C_{16:0}$ and $C_{18:0}$ probably relates to the differences in volatility of the analytes and the amounts injected. If we consider a typical trapped amount of analyte to be 200 µg of C then the proportion of cross contamination would range from 0.04 % to 13.6 %, which would have a significant impact on radiocarbon determinations for all range of sample ages as is it above the 0.1% contamination with infinite age carbon (Section 1.3.3.2). This clearly demonstrates a further source of contamination in PCGC and emphasizes the need for cleaning the instrument between trapping sequences.

Table 3-10: Details of successive cleaning tests and contents of the traps. Every test was split in two sequences with the PCGC. For the first sequence the standard solution injected to contaminate the instrument with the isolation of $C_{16:0}$ in the T1 and $C_{18:0}$ in the T2. The second sequence was injection of either standard solution either pure solvent. This table reports the content of the traps from the second sequence.

Test #	Cleaning capillaries	Trap design	Sample injected	Isolated in T1	$C_{16:0}$ in T1 (µg)	Isolated in T2	$C_{16:0}$ in T2 (µg)	$C_{18:0}$ in T2 (µg)
1	No	S-trap	Sdt Solution	N/A	1	$C_{16:0}$ FAME	316	61
2	Yes	S-trap	Sdt solution	N/A	0	$C_{16:0}$ FAME	270	0
3	No	S-trap	*n*-hexane	N/A	2	N/A	-	2
4	No	S-trap	*n*-hexane	N/A	1	N/A	-	11
5	No	S-trap	*n*-hexane	N/A	0.1	N/A	-	15
6	No	G-trap	*n*-hexane	N/A	38	N/A	-	19
7	Yes	S-trap	*n*-hexane	N/A	0	N/A	-	0
8	Yes	S-trap	*n*-hexane	N/A	0	N/A	-	0
9	Yes	S-trap	*n*-hexane	N/A	0	N/A	-	0

Repeating the analyses (by GC) described above after cleaning using the heat gun (Test 2, 6-9) confirms that this approach entirely eliminates any FAMEs condensed at the end of the capillaries (Figure 3-15b, d; Table 3-10).

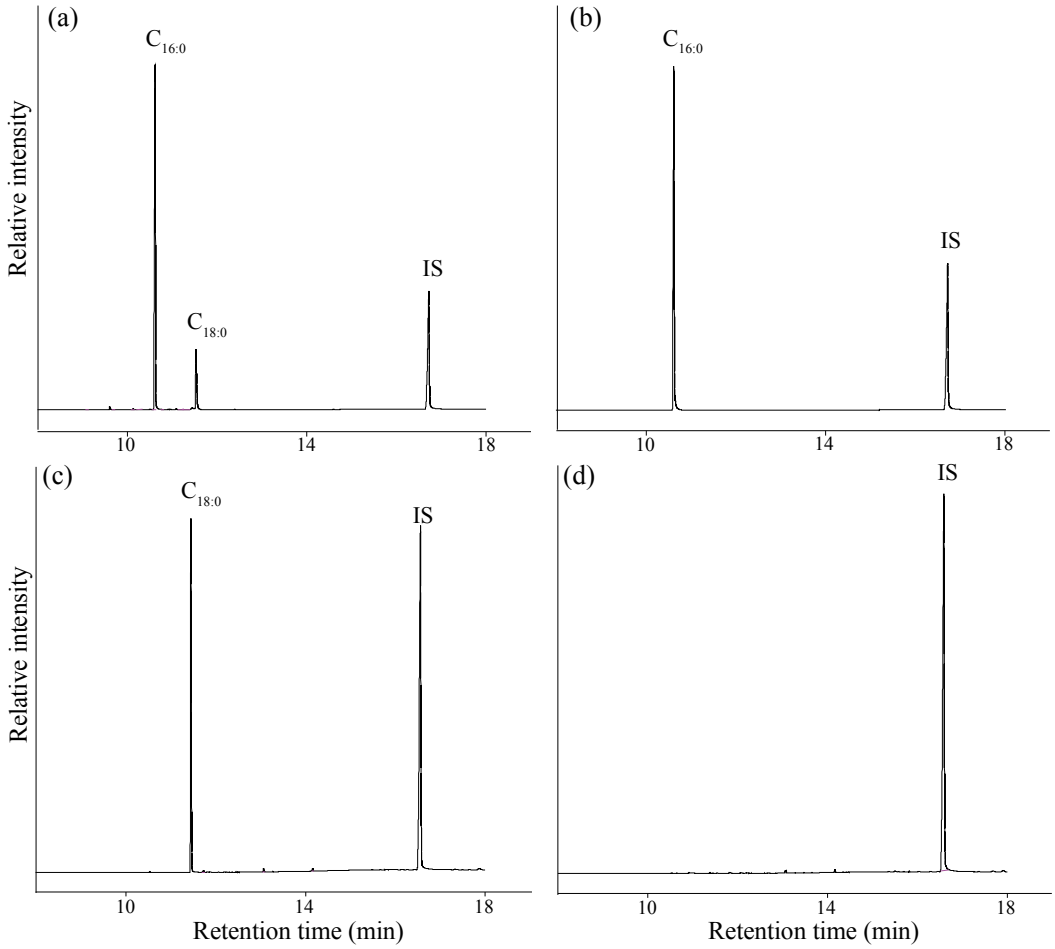

Figure 3-15: Partial gas chromatogram of the content of the trap T2 for (a) test 1, (b) test 2, (c) test 4 and (d) test 8. The IS corresponds to the internal standard. See Table 3-8 for detailed parameters of the different tests.

3.6.3 Evaluation of effects of cross contamination/cleaning by ^{14}C determinations

The heat cleaning method (and S-trap design) was then applied (similarly to Section 3.6.2) to TLEs of archaeological materials presenting the possibility to isolate $C_{16:0}$ and $C_{18:0}$ FAs in order to evaluate whether remaining contaminants, undetectable by GC analyses, are present at a level that could significantly affect radiocarbon determinations (Section 2.5.2.3).

3.6.3.1 Compound-specific dating of archaeological bog butter

First, the method was applied to FAs isolated from a bog butter (composed of purely of animal fats; details in Chapter 4) bulk dated from 3,069 ± 16 BP (Sections 2.2.2, 2.3.4.1; Figure 3-16). The bog butter extract was introduced to the PCGC immediately after isolation of the standard $C_{16:0}$ and $C_{18:0}$ FAME solution without cleaning to evaluate cross-contamination. The CSRA dates of the bog butter were determined as 2,985 ± 36 BP and 2,934 ± 37 BP for the $C_{16:0}$ and $C_{18:0}$ FAMEs, respectively which are each outside a 2σ range from the bulk date (Figure 3-16). This corresponds to ~2.6 % and ~3.5 % of contamination with modern FAMEs, respectively, for the $TC_{16:0}$ and $TC_{18:0}$ fatty acids, which is a significant level of contamination.

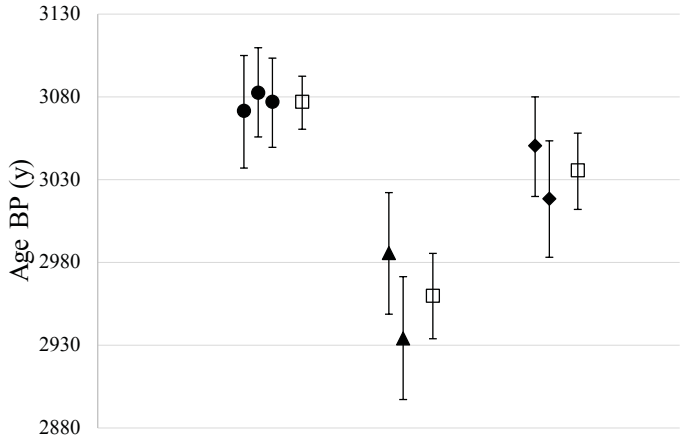

Figure 3-16: Bog Butter IB 1. Black dots are bulk dates, black triangle CSRA dates without instrument cleaning, black diamonds CSRA dates with instrument cleaning and white squares are weighted average. The errors associated with each point are the measurement errors.

Hence, the analysis was repeated after a heat gun was used to clean the capillaries to verify that no significant contamination is remaining and detectable by ^{14}C measurements. The fatty acids of the same bog butter were isolated and dated at 3,050 ± 30 BP and 3,018 ± 35 BP for the $C_{16:0}$ and $C_{18:0}$ homologies. Combining the measurements gave a date of 3,035 ± 22 BP, which is identical within a 2σ error to the bulk date (T' = 1.6, T'(5%) = 3.8, υ = 1; Figure 3-16), confirming that cleaning the capillaries improves accuracy.

3.6.3.2 Compound-specific dating of archaeological pottery vessels

The method described above was then applied to two archaeological pottery vessels (ROS-C-4678, ROS-C-4690), which TLE (> 1 $mg.g^{-1}$) was dominated by $C_{16:0}$ and $C_{18:0}$ FAs (Appendix 8), where the context was dated from articulated bones to 6,194 ± 15 BP on average (Denaire *et al.* 2017; details in Chapter 5). The FAMEs from the first pottery vessel (ROS-C-4690) were isolated using the PCGC immediately after analysing the bog butter and was dated at 4,943 ± 54 BP and 4,451 ± 48 BP for the $C_{16:0}$ and $C_{18:0}$ FA, respectively (Table 3-11; Figure 3-17).

Table 3-11: Radiocarbon dates on bones from the site Rosheim "Rittergass" (from Denaire *et al.* 2017) and on pottery vessels ROS-C-4690 and ROS-C-4678 from the same contexts.

References dates on bones			**CSRA on pottery vessel**				
Lab #	**Age ± 1σ (BP)**	**σ range**	**Sample**	**BRAMS #**	**$F^{14}C$ ± 1 σ**	**Age ± 1σ (BP)**	**σ range**
SUERC-46511	6,183 ± 34	*	**ROS-C-4690**	1144.1.1	0.5404 ± 0.0034	4,943 ± 54	X
OxA-27807	6,202 ± 30	*	**No cleaning**	1144.1.2	0.5749 ± 0.0033	4,451 ± 58	X
SUERC-46512	6,174 ± 34	*	**ROS-C-4678**	1145.1.1	0.4815 ± 0.0024	5,884 ± 42	X
OxA-27808	6,222 ± 31	*	**No cleaning**	1145.1.2	0.5155 ± 0.0025	5,330 ± 41	X
SUERC-46513	6,185 ± 34	*	**ROS-C4-678**	1145.1.1	0.4654 ± 0.0017	6,144 ± 31	*
Weighted average	**6,194 ± 15**		**cleaning**	1145.1.2	0.4641 ± 0.0018	6,167 ± 32	*

* identical within 1σ of the average on reference dates
** identical within 2σ of the average on reference dates
X not identical within 2σ of the average on refence dates

The dates of the two FAMEs were not identical within error and comparison with the associated date failed the χ^2 test at the 5 % level (T' = 1275.9, T'(5%) = 12.6, υ = 6). Following this, another pot extract (ROS-C-4678) was run on the PCGC and dated at 5,871 ± 42 BP and

5,323 ± 41 BP, respectively for the $C_{16:0}$ and $C_{18:0}$ FAs. Again, the measurements are younger in date than the associated bone dates and failed the χ^2 test at the 5 % level (T' = 420.3, T'(5%) = 12.6, υ = 6). Cross-contamination was significant in both traps. According to Ziolkowski and Druffel (2009), 40 repeated injections of sample ROS-C-4690, before the isolation of the sample ROS-C-4678 (supposedly of the same age), should have 'cleaned' the capillaries however, the radiocarbon determination demonstrated that significant contamination remained. It is, therefore, possible that instead of eliminating all chemical 'memory' from the previous trapping sequence, more material actually accumulates at the end of the capillary. The dating of a new extract of the pot ROS-C-4678 (pot ROS-C-4690 could not be re-sampled) was then repeated after using a heat gun to clean the capillaries (Table 3-11; Figure 3-17). The dates obtained on both FAs are identical within a 2-σ sigma error and combined to give a date of 6,156 ± 22 BP. The determinations are statistically identical to the dates from the associated articulated bones (T' = 3.9, T'(5%) = 12.6, υ = 6).

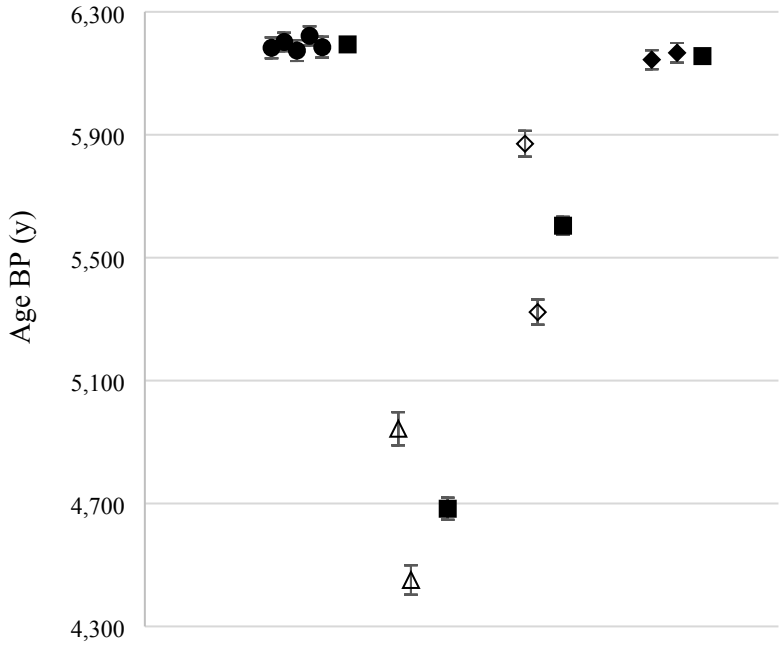

Figure 3-17: Black dots are associated dates on bones from the same context (Denaire *et al.* 2017), white triangles are CSRA dates on ROS-C-4690 without cleaning the instrument, white diamonds CSRA dates on ROS-C-4678 without cleaning the instrument, black diamonds CSRA dates on ROSC4678 with cleaning the instrument and black squares correspond to the weighted average. The error associated are the measurement errors.

3.6.4 Summary

It was shown that part of the analytes isolated remain in the cold-spots of the instrument in amount that would significantly affect ^{14}C analysis and this fraction is likely to increase with compounds of higher molecular weight. Furthermore it was highlighted that isolating the analyte through the instrument ten times to 'clean' the capillaries before fitting new traps is not a viable cleaning method despite its common use (e.g. Ziolkowski and Druffel 2009). The heat-based cleaning method was applied to modern and archaeological materials then evaluated by GC and ^{14}C determinations, which results showed no remaining contaminants in concentrations that significantly affect a radiocarbon measurement. The heat gun used as a cleaning method showed the advantages of being (i) fast, (ii) easy to use, (iii) extremely efficient and (iv) it preserves precious analytes.

3.7 Conclusion

This new protocol using PCGC for the isolation of FAs from lipid extracts of pottery vessels prior to ^{14}C determinations provides significant advantages, which are:

(i) The optimisation of method length to isolate 200 μg of C from one pottery extract in a day by the adoption of thicker film capillary GC columns and injection of more concentrated TLEs.

(ii) Identification and quantification of the exogenous C (i.e. degradation of GC column stationary phase and impurities co-eluting with the compounds isolated) during the isolation of single compounds using high field NMR.

(iii) The use of a new trap design allowing solventless recovery of isolated compounds from the traps, completely eliminating residual solvent contamination.

(iv) The use of a heat-assisted cleaning method for trap capillaries to eliminate memory effects and cross-contamination.

It was demonstrated that accurate and precise ^{14}C measurements are obtained from isolated compounds with the use of a new solventless trapping system and cleaning method; this constitutes a significant practical advance in CSRA of lipids isolated by PCGC.

Chapter 4.

CSRA archaeological materials and pottery vessels from well-dated sites

Chapter 4. CSRA of archaeological materials and pottery vessels from well-dated sites

4.1 Validating the new CSRA method

The groundwork studies by Stott *et al.* (2001, 2003) recognised how important it is to evaluate the CSRA method using known-age pottery vessels. This step is necessary to assess the reliability and reproducibility of the method prior to its application on unknown age samples. They carefully selected six British sites which were dated from the Early Neolithic to the Medieval ages by the style of the pots (West Cotton, Stanwick, Yarton, Eton Rowing Lake), by dendrochronology (Sweet Track) or by radiocarbon measurements (Hambledon Hill; Stott *et al.* 2003). In addition, these sites presented a span of ca. 5,000 years, and different burial environments (e.g. wetland, chalk, sand) allowing evaluation of the method on different preservation conditions of pottery vessels. However, for these studies the ^{14}C measurements failed to achieve the accuracy required and the method was not applied to unknown vessels. Hence, the establishment of the CSRA approach, or indeed any other technique, as an archaeological dating method requires a rigorous evaluation using know age reference materials. These reference materials used to evaluate dates from CSRA can be from (i) standard or archaeological materials which can be both reliably dated as bulk and as a single fraction and (ii) archaeological pottery vessels from securely dated contexts.

4.1.1 Use of standards and materials which can be bulk and CSRA dated

The first evaluation of the method was performed in Chapter 3 using modern standards (i.e. FAMEs). This approach has been widely used to estimate PCGC contamination for a range of biomarkers (e.g. Eglinton *et al.* 1996; Ziolkowski and Druffel 2009). For dating specific

materials (e.g. bones), archaeological samples of the same nature and a range of ages have been used. This approach works well for archaeological materials that can be both bulk and CSRA dated. The dates on both bulk and CSRA are identical on statistical basis if they pass the statistical χ^2 test introduced by Ward and Wilson (1978); see Section 4.5). For instance, Deviese *et al.* (2018) recently improved the current isolation protocol of hydroxyproline from collagen using preparative HPLC. They compared the bulk dates from the known age standard Mary Rose pig bone collagen and infinite age bones, to the single compound isolated by preparative HPLC. The hydroxyproline isolated yielded radiocarbon dates identical within a 2σ error to those of the bulk age.

In the case of archaeological pottery, however, the use of a bulk lipid date for assessment is not an option. Previous attempts to bulk date lipids (e.g. Hedges *et al.* 1992; unpublished data of J. Dunne and J. Smyth) did not meet the accuracy required, as these were not identical to reference measurements available. Generally, the dates obtained were 'too old' likely due to infinite age solvent remaining within the extract, supporting the need for a more robust method for radiocarbon dating lipids extracted from pottery vessels.

A unique archaeological material which provides the possibility for both bulk and CSRA dating of lipids (i.e. FAMEs) is the bog butters, which are archaeological fat hoards preserved in peat bogs (see Section 4.3, Earwood 1997; Berstan *et al.* 2004).

4.1.2 Use of pottery vessels from securely dated contexts

The direct evaluation of the CSRA method on pottery vessels requires the selection of artefacts from well-dated contexts, such as dendrochronology dated wood or articulated bones. In the case of dendrochronology, the deposition rate is precisely known. Thus, the radiocarbon measurements on tree rings which are used to build the terrestrial calibration curve (and

covering the year of construction) can be compared to the measurement from the potsherd (see Section 4.4.1). The ^{14}C ages determinations can, then, be calibrated and their contemporaneity tested in a model with known age gaps (Sections 2.5.3.5 and 4.4.1; Bronk Ramsey 1995, 2008; Bronk Ramsey *et al.* 2001).

In most cases, however, archaeological contexts are dated from bone collagen, grains, charred residues or charcoal and the deposition rate (e.g. use of pit for one or several generations) is not necessarily precisely known. In simple cases with one deposition event, to test the hypothesis that the CSRA and reference dates (from the same context) have the same true age the statistical χ^2 test introduced by Ward and Wilson (1978) is used (see Section 4.4.2). However, the evaluation of CSRA dates in a dated sequence can be more challenging. In the case of dating a succession of phases at sites presenting tight chronologies (e.g. Denaire *et al.* 2017), uncalibrated radiocarbon dates on successive phases can indeed pass the χ^2 test but may not represent the same event.

Chronological models are built using the relative age of archaeological artefacts (established by stratigraphy or seriation) and ^{14}C measurements to estimate as precisely as possible the phases, their length, and their boundaries (Bronk Ramsey 1995, 2008, 2009; Bronk Ramsey *et al.* 2010; Lee and Ramsey 2012). The statistical models allow the estimation of the probability of an event for appearing at a particular time, sometimes even at the level of a few decades (e.g. Bayliss *et al.* 2015; Jakucs *et al.* 2016; Denaire *et al.* 2017). Based on the hypothesis that the reference radiocarbon measurements are accurate, and the model based on them is valid, then such evaluation corresponds to a rigorous test which can be applied to the CSRA measurements to evaluate their accuracy. Thus, new CSRA dates, on potsherds, (not necessarily from the previously dated context) can be evaluated by including them in pre-existing models in a position defined by the stratigraphy (see Sections 4.4.3 and 4.4.4) or the

seriation. If accurate dates on pottery vessels are obtained then the revised model should give a similar output, with or without the dates on lipids extracted from the pottery vessels.

4.2 Aim and objectives

The overall aim of this chapter is to apply the method developed in Chapter 3 to archaeological pottery in order to demonstrate its validity. This chapter first focuses on testing the method by comparing compound-specific dates obtained from FAMEs to bulk radiocarbon dates from a range of archaeological bog butters. The second test focuses on dating pottery vessels from sites well-dated (i) dendrochronologically, using the example of the Sweet Track, England, (ii) from collagen at Takarkori Rock Shelter, Libya, (iii) from bones, charcoal and grains from a Neolithic occupation sequence at Çatalhöyük, Turkey, (iv) from charred pottery residues from Cliffs End Farm, England (Section 2.2.3). These sites were selected because they include pottery vessels (with high lipid concentrations) dated indirectly by comparison to other materials from the same site and stratigraphic contexts (considered homogenous in time) and thus serve as reference pottery assemblages for validation of the method. To put it simply this will confirm whether identical ages can be obtained from lipids, preserved in pottery, to those obtained from wood, charcoal, collagen, seeds, charred residues etc. In addition, the sites chosen comprise settlements with ages ranging from ca.7,400 BP to 2,500 BP, and different burial environments, including wetland and arid areas.

4.3 Radiocarbon dating archaeological bog butters

4.3.1 Bog butter description

Bog butters are found as singly deposited hoards recovered in amounts up to 50 kg, and are commonly recovered from Irish, Scottish and Norwegian peat bogs (Earwood 1991, 1997). The

Irish ones have been shown to be pure fats, largely butter (Berstan 2002, Berstan *et al.* 2004). They are composed of TAG, DAGs, free fatty acids, dominated by the $C_{14:0}$, $C_{16:0}$ and $C_{18:0}$ FAs, but also proteinaceous material and free amino acids (Thornton *et al.* 1970; Morgan *et al.* 1973; Cronin *et al.* 2007; Berstan 2002; Berstan *et al.* 2004). Critically, due to their purity and varying age (from Bronze Age to Medieval times; Earwood 1997) they present a unique opportunity to rigorously validate the CSRA dating method, as FAs can be isolated by PCGC, and they can be directly radiocarbon dated and used as 'known age' standards for CSRA.

4.3.2 Comparison of bulk and CSRA determinations

A total of 6 bog butters were selected for the study. In order to test the homogeneity of the archaeological fats prior to CSRA dating, bulk ^{14}C measurements of 4 bog butters were performed in triplicate (Sections 2.3.4.1, 2.3.4.2). The triplicate dates of each bog butter were found to be statistically identical (Table 4-1, Figure 4-1). The fatty acids of the 6 bog butters that yielded bulk dates of 3,069 ± 16 BP (IB1, T = 0.0, T'(5%) = 5.9, υ = 2), 3,311 ± 26 BP (IB3), 1,153 ± 25 BP (IB6), 1,971 ± 25 BP (IB12, T = 0.1, T'(5%) = 5.9, υ = 2), 2,193 ± 15 BP (IB18, T = 1.0, T'(5%) = 5.9, υ = 2) and 509 ± 15 BP (IB19, T = 0.4, T'(5%) = 5.9, υ = 2) were then isolated using PCGC.

The individual ^{14}C dates on the $C_{16:0}$ and $C_{18:0}$ FAs were identical within a 2σ error for each bog butter confirming uniformity of measurements for two different compounds from the same find (Table 4-1, Figure 4-1). Two of the bog butters (IB18 and IB19) were re-sampled, methylated and CSRA performed a second time; no significant differences in the dates were detectable, as the χ^2 test at the 5 % level was successfully applied in both cases, confirming excellent reproducibility of the method.

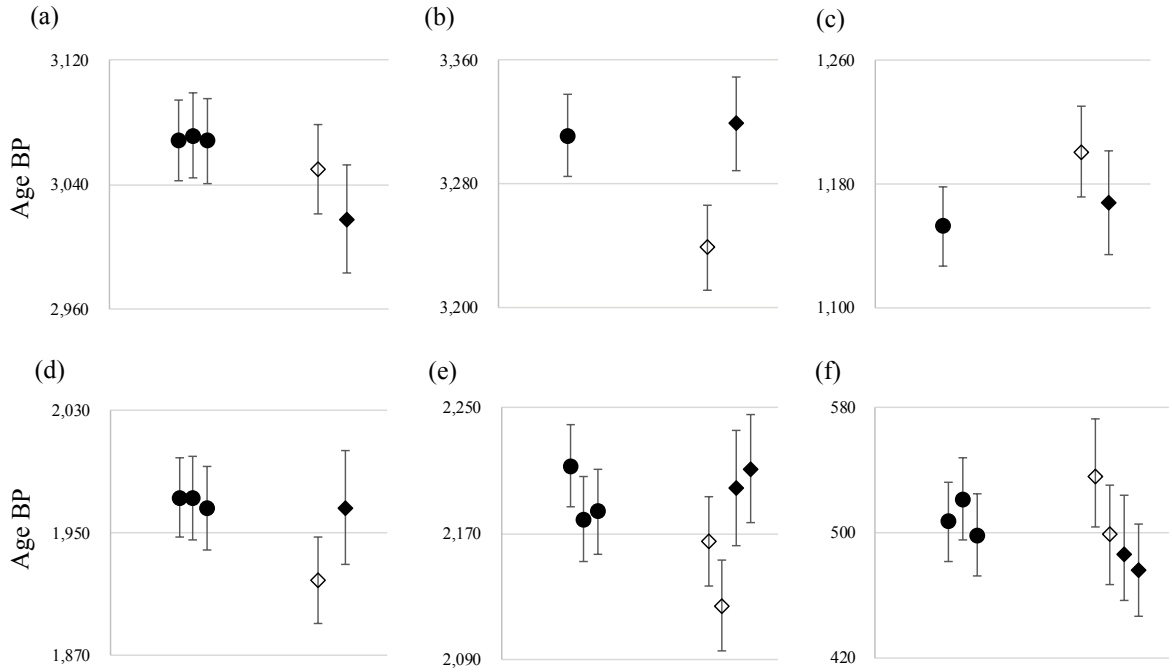

Figure 4-1: Bulk and CSRA measurements (in years BP) for (a) IB1, (b) IB3, (c) IB6, (d) IB12, (e) IB18 and (F) IB19. Dots correspond to bulk dates and diamonds to CSRA dates. The white diamonds are dates determined from $C_{16:0}$ and black diamonds are dates from $C_{18:0}$ FAs. The error bars correspond to the 1σ analytical uncertainty.

Comparison of the weighted averages of the bulk dates with single ^{14}C determinations on FAMEs showed they were identical within 1 or 2σ error, with one exception, IB18-$C_{16:0}$ (BRAMS-1102.4.1) for which the ^{14}C measurement was just outside the 2σ error of the weighted average (2,193 ± 15 BP). All bulk and CSRA determinations for each of bog butter were subjected jointly to the χ^2 test at the 5 % level, which they all passed successfully (IB1, T' = 1.9, T'(5%) = 7.8, υ = 4; IB3, T' = 4.8, T'(5%) = 5.9, υ = 2; IB6, T' = 1.6, T'(5%) = 5.9, υ = 2; IB12, T' = 1.8, T'(5%) = 9.5, υ = 4; IB18, T' = 6.7, T'(5%) = 12.6, υ = 6; IB19, T' = 2.4, T'(5%) = 12.6, υ = 6), indicating statistically identical measurements between bulk and CSRA with an acceptable level of scatter (0.0025). Thus, there is extremely good agreement between bulk and CSRA dates; this is further emphasized by plotting the CSRA dates against bulk dates (Figure 4-2).

Table 4-1: Bulk and compound-specific radiocarbon dates measured on six bog butters with ages ranging from ~3,000 to 500 BP.

Bulk dates						CSRA dates						
Sample	**BRAMS #**	**mCO_2 (µg)**	**$F^{14}C \pm 1\sigma$**	**Age ± 1σ (BP)**	**σ range**	**Sample**	**BRAMS #**	**mCO_2 (µg)**	**$F^{14}C \pm 1\sigma$**	**Age ± 1σ (BP)**	**σ range (FAs)**	**σ range (bulk)**
IB1	1087.1.1	990	0.6825 ± 0.0022	3,068 ± 26	*	**IB1-$C_{16:0}$**	1087.4.1	287	0.6841 ± 0.0024	3,050 ± 30	•	*
IB1	1087.1.2	994	0.6823 ± 0.0024	3,072 ± 28	*	**IB1-$C_{18:0}$**	1087.4.2	173	0.6868 ± 0.0028	3,018 ± 35		**
IB1	1087.1.3	996	0.6825 ± 0.0024	3,068 ± 28	*							
Weighted average			**0.6824 ± 0.0013**	**3,069 ± 16**		**Weighted average**			**0.6853 ± 0.0018**	**3,035 ± 35**		*
IB3	1089.1.1	983	0.6622 ± 0.0022	3,311 ± 26		**IB3-$C_{16:0}$**	1089.2.1	-	0.6682 ± 0.0022	3,239 ± 28	••	**
						IB3-$C_{18:0}$	1089.2.2	-	0.6616 ± 0.0024	3,319 ± 31		*
						Weighted average			**0.6650 ± 0.0016**	**3,288 ± 16**		*
IB6	1092.1.1	998	0.8663 ± 0.0027	1,153 ± 25		**IB6-$C_{16:0}$**	1092.2.1	193	0.8611 ± 0.0029	1,201 ± 29	•	**
						IB6-$C_{18:0}$	1092.2.2	113	0.8647 ± 0.0034	1,168 ± 34		*
						Weighted average			**0.8628 ± 0.0034**	**1,172 ± 17**		*
IB12	1096.1.1	995	0.7822 ± 0.0025	1,974 ± 26	*	**IB12-$C_{16:0}$**	1096.2.1	240	0.7875 ± 0.0034	1,919 ± 37	•	**
IB12	1096.1.2	993	0.7823 ± 0.0026	1,973 ± 27	*	**IB12-$C_{18:0}$**	1096.2.2	110	0.7829 ± 0.0037	1,967 ± 40		*
IB12	1096.1.3	988	0.7829 ± 0.0026	1,966 ± 27	*							
Weighted average			**0.7825 ± 0.0015**	**1,971 ± 16**		**Weighted average**			**0.7853 ± 0.0025**	**1,961 ± 13**		*
IB18	1102.1.1	974	0.7592 ± 0.0024	2,213 ± 26	*	**IB18-$C_{16:0}$**	1102.3.1	343	0.7637 ± 0.0026	2,165 ± 29	•	*
IB18	1102.1.2	991	0.7624 ± 0.0026	2,179 ± 27	*	**IB18-$C_{18:0}$**	1102.3.2	141	0.7605 ± 0.0033	2,199 ± 37		*
IB18	1102.1.3	997	0.7620 ± 0.0026	2,184 ± 27	*	**IB18-$C_{16:0}$**	1102.4.1	423	0.7676 ± 0.0026	2,124 ± 29	••	X
						IB18-$C_{18:0}$	1102.4.2	123	0.7594 ± 0.0031	2,211 ± 35		*
Weighted average			**0.7612 ± 0.0015**	**2,193 ± 15**		**Weighted average**			**0.7623 ± 0.0020**	**2,172 ± 16**		*
IB19	1103.1.1	997	0.9388 ± 0.0030	507 ± 25	*	**IB19-$C_{16:0}$**	1103.2.1	-	0.9355 ± 0.0041	536 ± 37	•	*
IB19	1103.1.2	999	0.9371 ± 0.0031	521 ± 26	*	**IB19-$C_{18:0}$**	1103.2.2	150	0.9413 ± 0.0042	486 ± 38		*
IB19	1103.1.2	995	0.9399 ± 0.0031	498 ± 26	*	**IB19-$C_{16:0}$**	1103.3.1	161	0.9398 ± 0.0035	499 ± 32	•	*
						IB19-$C_{18:0}$	1103.3.2	207	0.9424 ± 0.0033	476 ± 29		**
Weighted average			**0.9386 ± 0.0018**	**509 ± 15**		**Weighted average**			**0.9399 ± 0.0018**	**503 ± 11**		*

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ
* measurement identical within 1σ of the weighted average of the bulk dates for individual bog butters
** measurement identical within 2σ of the weighted average of the bulk dates for individual bog butters
X measurement non-identical within a 2σ range of the weighted average of the bulk dates for individual bog butters

Over a 3,000 year range the data points are described by a linear function, y = 0.9875x + 8.7082, R^2 = 0.999. The slope indicates almost a 1/1 ratio for CSRA/bulk measurements, in addition the line intercepts close to the origin at ~9 years, which is within the measurement error of the AMS, suggesting no significant offsets exist within the CSRA measurements.

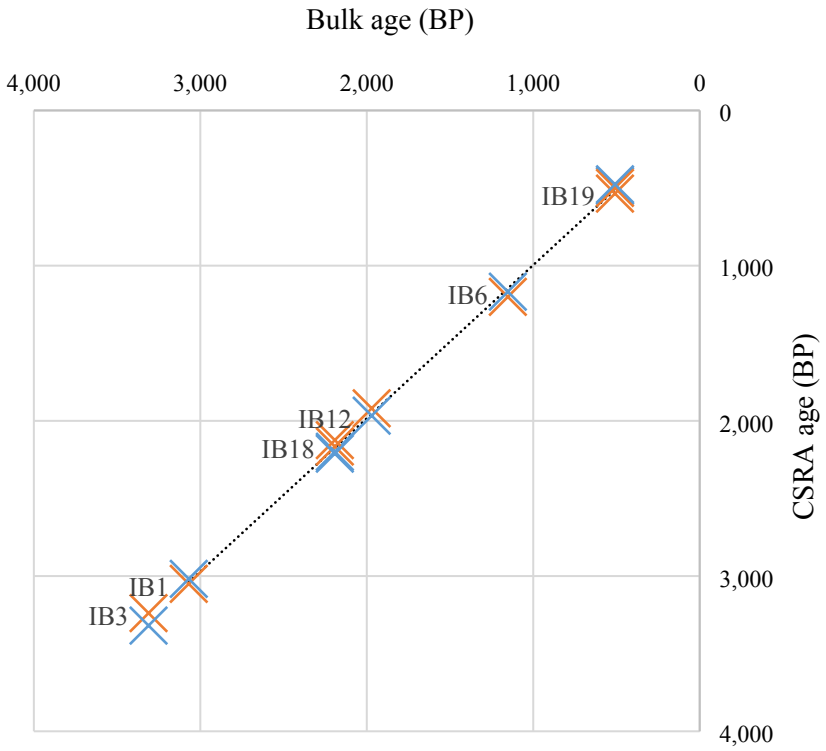

Figure 4-2: CSRA measurements (in years BP) plotted against the weighted average of bulk measurements for 6 bog butters of age ranging between 3,000-500 BP. The $C_{16:0}$ FAs dates are represented by orange crosses and $C_{18:0}$ FAs by blue crosses. Dashed line corresponds to the linear trendline modelled for the data points (y = 0.9875x + 8.7082; R^2 = 0.999).

4.3.3 Summary

These results demonstrate the possibility for generating radiocarbon dates on single FAs statistically identical to the bulk fats using the new S-traps combined with cleaning of the capillaries between trapping sequences using the new heat gun method. The data indicate no significant contamination is associated with the isolation procedure which would prevent the generation of statistically identical dates on two single compounds isolated from the same

matrix. Therefore, one important criterion used as an internal quality control to evaluate the accuracy of CSRA measurements in the rest of this thesis is the generation of $C_{16:0}$ and $C_{18:0}$ FAs dates which are identical within a 2σ error and can be combined as explained in Section 2.5.3.4.

4.4 Radiocarbon dating of pottery vessels from diverse locations

4.4.1 British Neolithic pottery vessels from the Sweet Track

4.4.1.1 Site description

The Sweet Track (SW), located in a wetland area between the Polden Hills and Westhay Island in the Somerset Levels (UK), is one of the earliest known elevated wooden trackways (ca. 2.1 km in length) in Europe (Figure 4-3; Coles and Coles 1986; Hillam *et al.* 1990). Its construction was dendrochronologically dated from winter 3,807 to summer 3,806 cal BC. Some parts of the trackway showed repairs between 3,804 and 3,800 cal BC (Hillam *et al.* 1990). It is suggested that the Sweet Track was not in use for more than a decade before being overwhelmed with reeds and water (Hillam *et al.* 1990). Pottery vessels (as complete or fragmented form), recovered alongside the track next to post, lie in the early Neolithic fine ware and carinated bowl tradition in southern Britain (Coles and Orme 1984), thus are clearly associated with the construction and use of the track.

A total of 13 potsherds from 9 pottery vessels recovered alongside the trackway were subjected to lipid residue analysis, revealing suitable concentrations of lipids for radiocarbon dating (Smith 1976; Coles and Orme 1984; Berstan *et al.* 2008). The precise dendrochronology date, short use of the trackway, and the preservation of pottery with lipid residues makes it a reference site of exceptional importance.

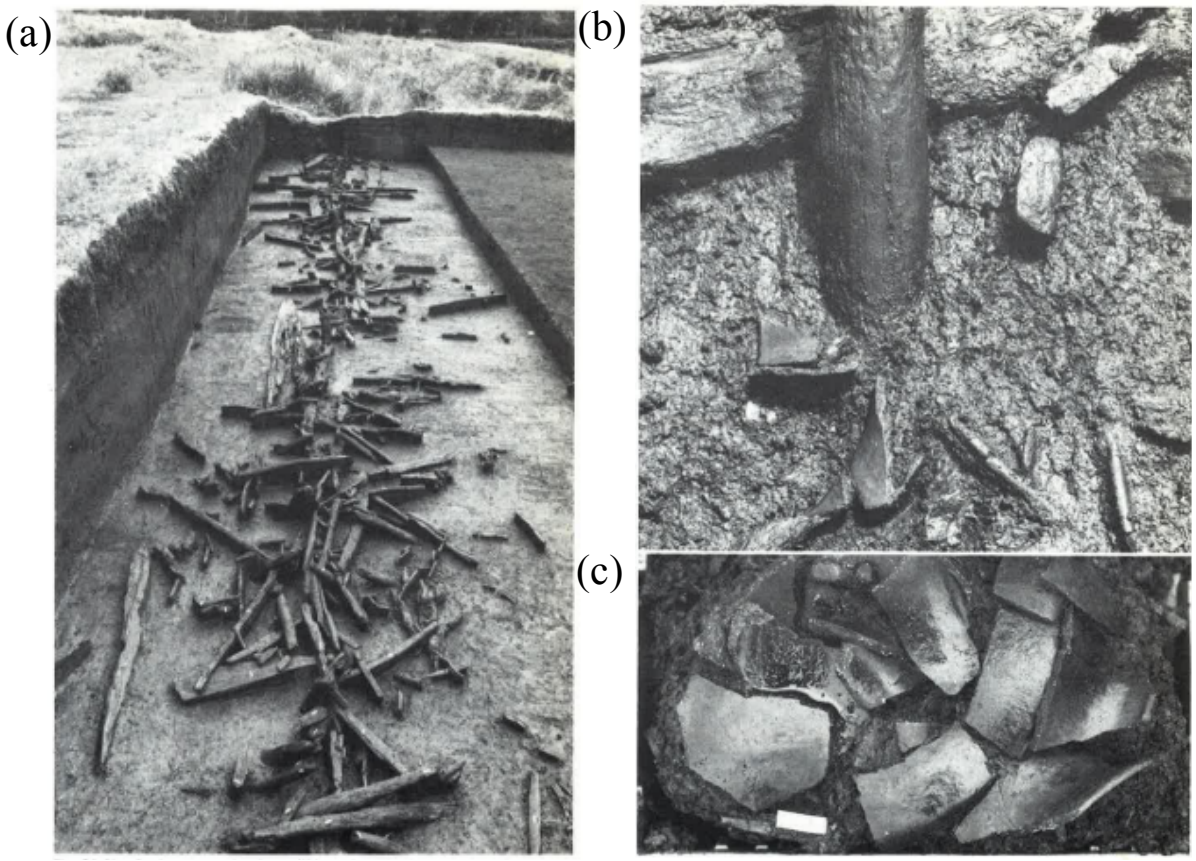

Figure 4-3: (a) Excavation of the Sweet Track at the archaeological site, (b) detail on potsherds from one pottery vessel found next to the rail and (c) a concentration of broken pottery found at the site. From Coles and Orme (1984, Figures 23, 57, and 58 respectively for (a), (b) and (c)).

4.4.1.2 CSRA determinations

Two vessels from the Sweet Track exhibiting high lipid concentrations of 13.8 (SW1) and 4.9 $mg.g^{-1}$ (SW2) were previously dated by Berstan *et al.* (2008), however, the dates obtained were younger by ca. 200 years than the construction of the trackway (Table 4-2; Appendix 2). The same potsherds were re-sampled and CSRA dated with the new method (Table 4-2).

The new dates are identical within a 2σ error for both fatty acids on each of the vessels. The combined measurements are 5,110 ± 25 for SW1 and 5,092 ± 26 for SW2 (T' = 0.0, T'(5%) = 3.8, υ = 1 for both). The measurements on the two pottery vessels are thus statistically consistent. The new dates are significantly older than those obtained by Berstan *et al.* (2008)

and presents higher precision (Table 4-2; Figure 4-4). The CSRA method developed in Chapter 3 therefore has provided more consistent results on the two vessels compared to the previous method.

Table 4-2: Compound-specific radiocarbon dates measured on two pottery vessels associated with the Sweet Track obtained by Berstan *et al.* 2008 (OxA dates) and re-evaluated within the context of this thesis (BRAMS dates).

Sample	Lab #	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	Calibrated age (95% prob. BC)	σ range
SW1-$C_{16:0}$	OxA-V-1045-17	883	0.5400 ± 0.0035	4,950 ± 50	3,932-3,642 BC	••
SW1-$C_{18:0}$	OxA-V-1045-18	996	0.5450 ± 0.0035	4,870 ± 50	3,776-3,532 BC	
SW1-$C_{16:0}$	BRAMS-1520.1.1	266	0.5297 ± 0.0019	5,105 ± 33	3,972-3,800 BC	•
SW1-$C_{18:0}$	BRAMS-1520.1.2	347	0.5290 ± 0.0019	5,114 ± 32	3,978-3,800 BC	
SW2-$C_{16:0}$	OxA-X-850-13	400	0.5510 ± 0.0040	4,790 ± 60	3,694-3,376 BC	••
SW2-$C_{18:0}$	OxA-V-1045-19	1026	0.5430 ± 0.0035	4,910 ± 50	3,798-3,542 BC	
SW2-$C_{16:0}$	OxA-X-850-14	1140	0.5460 ± 0.0040	4,860 ± 60	3,780-3,520 BC	•
SW2-$C_{18:0}$	OxA-V-1046-5	614	0.5430 ± 0.0050	4,900 ± 80	3,942-3,520 BC	
SW2-$C_{16:0}$	BRAMS-1521.1.1	138	0.5307 ± 0.0023	5,089 ± 38	3,966-3,796 BC	•
SW2-$C_{18:0}$	BRAMS-1521.1.2	446	0.5304 ± 0.0018	5,094 ± 32	3,966-3,798 BC	

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ

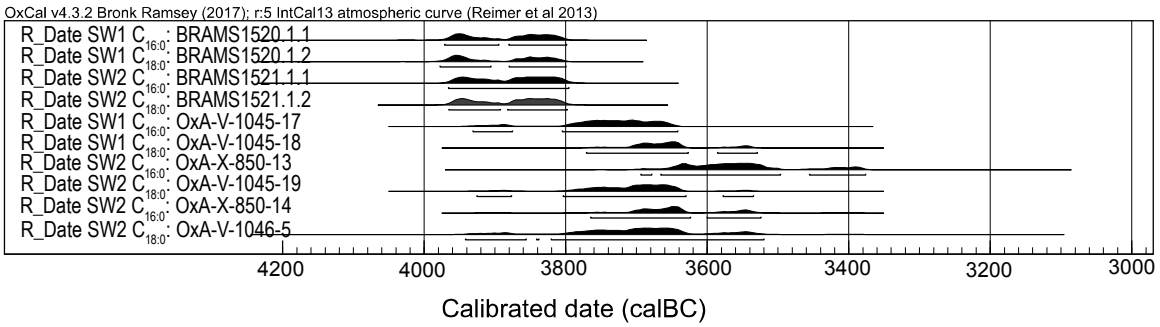

Figure 4-4: Probability distribution of an event to occur at a particular time for radiocarbon dates on SW1 and SW2 obtained in this thesis and by Berstan *et al.* (2008) in OxCal v4.2 (Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

4.4.1.3 Comparison with dendrochronological dates

The IntCal13 calibration curve is compiled using three measurements on oak trees covering the year 3,807/6 BC (Table 4-3; Pearson *et al.* 1986; Stuiver and Becker 1993; Stuiver *et al.* 1998b; de Jong *et al.* 1986, 1989; Reimer *et al.* 2013).

Table 4-3: Dendrochronological measurements which cover the years 3087/6 BC in the IntCal13 calibration curve. The error associated with the measurements are counting statistics modified by the error multiplier suggested by Reimer *et al.* 2004; Table 1).

Sample	Lab #	Age ± 1σ (BP)	Dendrochronological age (BC)	References
German Oak	QL-11528	5,083 ± 17	3,804-3,805	Stuiver *et al* 1993,1998
German Oak	GrN-9024	5,058 ± 18	3,807 (growth)	De Jong *et al.* 1986,1989
Irish oak	UB-1198	5,020 ± 23	3,809-3,810	Pearson *et al* 1996

The combined ^{14}C measurements of lipids from pottery vessels are compatible with the dendrochronological date of the Trackway (Figure 4-5). They are also statistically indistinguishable from those included in the IntCal13 calibration curve (T' = 9.0, T'(5%) = 9.5, υ = 4). When calibrated, the measurements from the lipids show good agreement with those covering the year 3,807/6 BC in (Acomb = 50.9, An = 31.6, n = 5; Figure 4-5; Bronk Ramsey *et al.* 2001) and have good individual agreements (SW1, A: 74; SW2, A: 102).

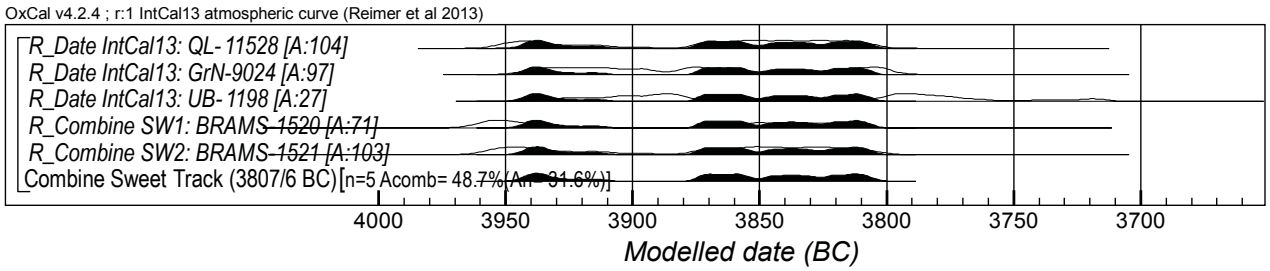

Figure 4-5: Comparison of the tree-rings dates covering the year 3807/6 BC in the calibration curve (IntCal; Reimer *et al.* 2013) and dates on fatty acids isolated from pottery vessels recovered from adjacent to the Sweet Track. The probability distributions plotted outline correspond to the simple radiocarbon calibration and the black ones the calibrated distribution with the model used, the last distribution corresponding to the output of the model. Courtesy of A. Bayliss (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

4.4.1.4 Summary

The new radiocarbon dates performed on lipids extracted from pottery vessels associated with the Sweet Track show older values than those achieved previously by Berstan *et al*. (2008). Residual solvent in the FAs would likely have shifted the dates toward older values. It is known (according to archive notes) that the potsherds were extracted in 2008, using PCGC, after

replacing the capillaries, which prevented the issue of cross-contamination. Therefore, it is likely that problems encountered were due to the exposure of isolated analytes to modern contaminants during the long handling delay between their isolation in traps and graphitisation (as suggested in Chapter 3).

The accuracy of the new dates on the lipids extracted from pottery vessels is supported by their ^{14}C measurements being statistically indistinguishable to those on oak timbers, reflecting their contemporaneity with the construction of the Sweet Track in 3,807/6 BC. This constitutes the accurate dating of lipids extracted from pottery vessels preserved in a wetland burial environment.

4.4.2 Libyan Neolithic pottery vessels from Takarkori Rock Shelter

4.4.2.1 Site description

Takarkori Rock Shelter (TAK) is situated in the Acacus Mountains in South East Libya and contains an (approximatively) 5,000 years stratigraphic sequence, deposited during the Late Holocene starting with the Late Acacus period (8,900 to 7,400 BP) followed by the Early (7,400-6,400 BP), Middle (6,100-5,000 BP) and Late (5,000-3,500 BP) Pastoral periods (Figure 4-6; di Lernia *et al.* 2012; di Lernia and Tafuri 2013; Biagetti and di Lernia 2013). The deposits, preserved in an arid environment, show layers of loose sand, organic sand, ash or charcoal. The long stratigraphic sequence revealed exceptional preservation of plant/seeds remains, basket but also rich lipid preservation in pottery vessels (di Lernia *et al.* 2012; Dunne *et al.* 2012; Mercuri *et al.* 2018). Numerous radiocarbon dates on bone collagen, dungs, coprolites, soils and seeds from different features were used to reconstruct the site chronology (Cherkinsky and di Lernia 2013; Mercuri *et al.* 2018).

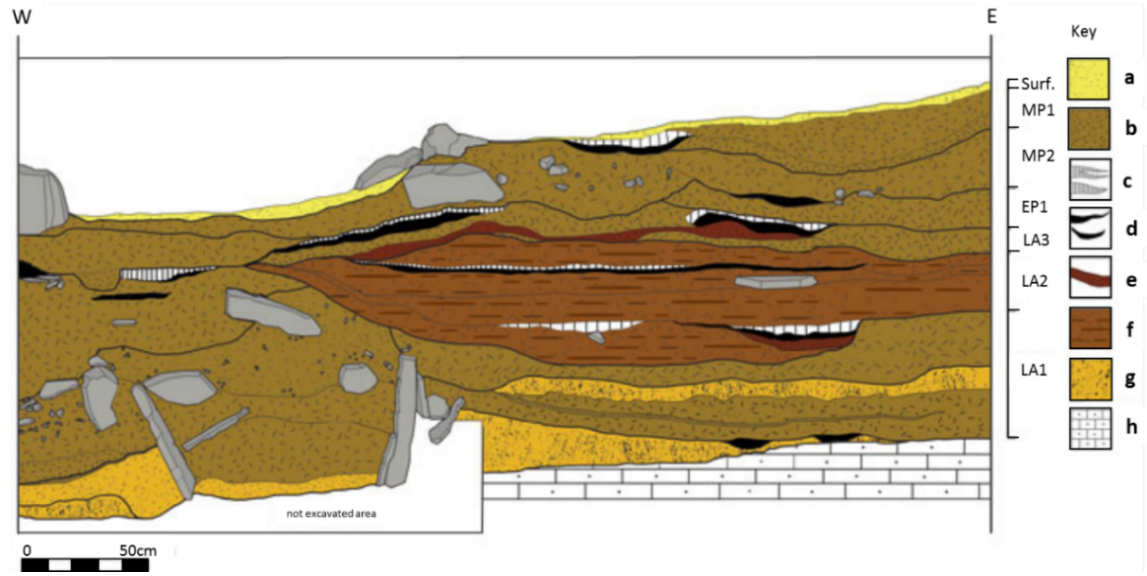

Figure 4-6: Stratigraphic sequence at Takarkori Rock Shelter (MP = Middle Pastoral, EP = Early Pastoral, LA Late Acacus) with (a) loose sand, (b) organic sand, (c) ash, (d) charcoals, (e) burnt ground, (f) house floor, (g) Coarse sand, (h) bebrock). From Biagetti and di Lernia (2013), Figure 7.

4.4.2.2 CSRA determinations

Two pottery vessels from the MP period at Takarkori Rock Shelter, previously bulk lipid dated (solvent extracted according to Evershed *et al.* (1990), dried in vacuum desiccator and transfer to tin capsule according to Berstan *et al.* (2008), unpublished data of J. Dunne), were selected (Table 4-4; ORA details in Appendix 3-1).

Table 4-4: Bulk and compound-specific radiocarbon dates on lipid extracted from pottery vessel from the site of Takarkori Rock Shelter.

Sample	Context	Laboratory #	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range
TAK 21-Bulk	25, T23	OxA-25767	-	-	5,772 ± 33	-
TAK 21-$C_{16:0}$	25, T23	BRAMS-1522.1.1	547	0.5130 ± 0.0017	5,362 ± 33	•
TAK 21-$C_{18:0}$	25, T23	BRAMS-1522.1.2	322	0.5150 ± 0.0018	5,331 ± 32	
TAK 1572-Bulk	245, S33	OxA-25769	-	-	7,176 ± 36	-
TAK 1572-$C_{16:0}$	245, S33	BRAMS-1523.1.1	685	0.5301 ± 0.0018	5,099 ± 38	•
TAK 1572-$C_{18:0}$	245, S33	BRAMS-1523.1.2	429	0.5319 ± 0.0018	5,071 ± 32	

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ

The CSRA dates on both FAs are identical within error for both potsherds, giving an average date for TAK21 of 5,346 ± 25 BP (T' = 0.5, T'(5%) = 3.8, υ = 1) and TAK1572 of 5,085 ± 25

BP (T' = 0.3, T'(5%) = 3.8, υ = 1). The new CSRA dates are considerably younger than the bulk dates obtained previously, suggesting the latter were contaminated with fossil carbon which could be associated with the TLEs. Here, fossil carbon could likely come from the incomplete removal of the solvent used for extraction or the contribution of plasticizers at concentrations not detected by GC-MS analysis (Dunne 2014).

4.4.2.3 Comparison with reference radiocarbon dates

The MP period at the site of Takarkori was dated between 6,090 ± 60 BP (GX-30324) for the oldest and 4,970 ± 25 BP (UGAMS#8707) for the youngest layer (reference dates in Appendix 3-2; Cherkinsky and di Lernia 2013). The potsherd TAK21 came from the layer 25, dated by a cattle collagen sample to 5,340 ± 50 BP (UGAMS-01841; Cherkinsky and di Lernia 2013) which is statically identical to the date on lipids of 5,346 ± 25 BP (T' = 0.0, T'(5%) = 3.8, υ = 1; Figure 4-7).

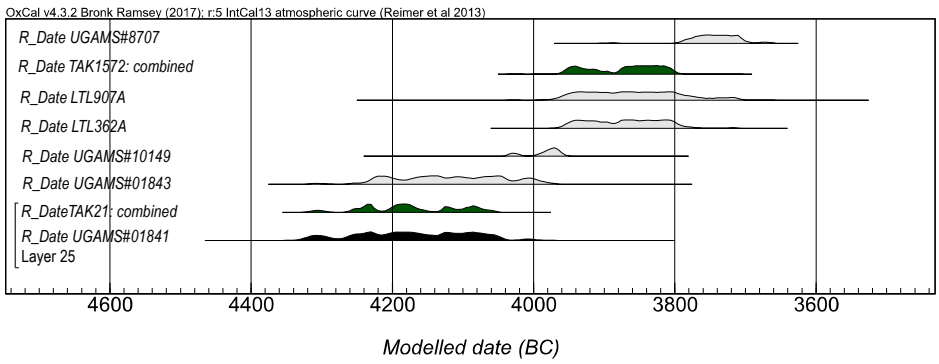

Figure 4-7: Probability distribution of reference dates for the Middle Pastoral period and dates from lipids extracted from potsherds. The distributions plotted in green correspond to the pottery vessels, in black to the reference date of layer 25 and in grey other dates available for the MP period (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

The potsherd TAK1572 came from the layer 245 which was unfortunately not dated. However, the range of calibrated dates on the lipids are in agreement with known MP period dates (Figure 4-7).

4.4.2.4 CSRA determinations of archaeological seeds?

Well-preserved archaeological seeds were found at the site and showed high lipid concentrations (>500 $\mu g.g^{-1}$ of seed; Appendix 3-3, Dunne 2014; Mercuri *et al.* 2018). Theoretically, bulks dates on the seeds and CSRA dates of their lipids should, as for the bog butters, give statistically identical ^{14}C dates. A sufficient quantity of *Sorghum* seeds was available to attempt this test of the CSRA method. The seeds were bulk dated in another laboratory to 7,930 ± 30 BP (UGAMS#8708) and again in the BRAMS facility to 7,998 ± 30 BP (Section 2.3.4.4).

However, lipid extraction of the seeds (ca. 50 mg) did not provide enough lipid far a sufficient target size. The target containing 71 µg of C was measured at a very low current. It was dated to 7,592 ± 38 BP (outside of a 2σ range of the bulk date), however, due to the small C size (χ^2 value on counting statistics too high) this result is not reliable and should be disregarded. For amount of C below 100 µg, the use of gas ion source would be required, and size-dependant measurements as performed Section 3.3.1 would need to be investigated.

4.4.2.5 Summary

The CSRA on pottery vessels agree with known dates of the MP period at the site. In addition, layer 25 showed indistinguishable dates for both pottery and bone collagen. The results obtained were significantly different from the bulk lipid dates previously obtained from the same sherds, demonstrating better accuracy of the CSRA method compared to bulk lipid dating. This confirms that lipids from pottery vessels, preserved in an arid area, can be accurately dated.

There is likely potential for CSRA dating of archaeological seeds, however, in this instance, this failed due to an insufficient amount of C being extracted from the seeds. This confirms that CSRA requires (i) more starting material than for a bulk date, (ii) more preparation time and (iii) good lipid preservation and concentration. In the case of well-preserved seeds, a bulk date is reliable and not 'difficult' to generate thus, there is no legitimate requirement to CSRA date seeds, considering the amount of material needed to start with.

4.4.3 Turkish Neolithic pottery vessels from Çatalhöyük East

4.4.3.1 Site description

The site of Çatalhöyük located in central Anatolia consisted of an early to late Neolithic occupation covering an area of 13 ha and, beginning in the 1960's (Mellaart 1962), the site has been excavated by several different teams. The site includes contexts dating from about 8,100 BP, which is the earliest Neolithic site in Central Anatolia and the earliest outside the area of Levant and Mesopotamia (Bayliss *et al.* 2015). It has also revealed the oldest clay pottery in the region and could be the loci of the manufacture and spread of pottery across Europe and West Asia (Bayliss *et al.* 2015).

Much of the late Neolithic contexts were destroyed by post-Neolithic activities, however, the late Neolithic features excavated at the East Mound in the TP (Team Poznan) area survived and have since been the object of a dating program (Marciniak *et al.* 2015). Features presenting a vertical stratigraphy over 6 levels (M to R) were selected for dating, with the aim of modelling the occupation timeframe using Bayesian statistics. A total of 50 radiocarbon measurements were recorded and incorporated into the model (Appendix 4-1 and 4-2), 15 of which showed an old wood effect and 6 of which were probably redeposited, curated, residual or reworked. The model had a good agreement (A_{model}: 63) and showed settlement occupation during the

7th millennium BC, thereby representing the oldest site investigated in this thesis. Pottery vessels recovered from all levels were studied for ORA and revealed the presence of ruminant adipose fats (Roffet-Salque and Evershed In press).

4.4.3.2 CSRA determinations

The adsorbed lipid residues of a total of 15 pottery vessels from the levels M to R of the TP were subjected to radiocarbon dating (Table 4-5; ORA details in Appendix 4-3). Lipid preservation at the site was quite low. Of the 15 pottery vessels selected (i.e. 29 targets) 5 did not contain enough C for graphitisation and 7 targets yielded low amount of C and, therefore, measured at too low current (counting statistics failed χ^2 test) to obtain reliable ^{14}C measurements. The data from these targets were not included.

Statistically identical pairs of measurements (2σ range) were obtained on FAs extracted from 4 pottery vessels, TP.M17 (T' = 1.9, T'(5%) = 3.8, υ = 1), TP.N10 (T' = 2.1, T'(5%) = 3.8, υ = 1), TP.O23 (T' = 3.1, T'(5%) = 3.8, υ = 1), TP.P.13 (T' = 2.4, T'(5%) = 3.8, υ = 1). Only one pot extract failed the test (TP.R09; T' = 27.8, T'(5%) = 3.8, υ = 1) suggesting a contamination of the analytes during the procedure. The remaining lipid extracts only generated one target (either $C_{16:0}$ or $C_{18:0}$) with sufficient carbon for dating, consequently, the internal quality control based on the statistical identicality of the two FAs dates was not available for those extracts. Except for low C size targets, the quality of ^{14}C measurements on each processed standard analysed alongside the FAs (Sections 2.2.1, 2.4.7, 2.4.9) suggests no constant contamination during the procedure affecting CSRA dates.

Table 4-5: Compound-specific radiocarbon dates measured on fatty acids extracted from pottery vessels from the site of Çatalhöyük East.

Sample	BRAMS #	Unit #	Context	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range	Comments	Reference
TP.M17-$C_{16:0}$	1654.1.1	17670	Sp.420	191	0.4011 ± 0.0020	7,338 ± 42	••	Included	Poz-40795
TP.M17-$C_{18:0}$	1654.1.2	17670	Sp.420	726	0.3972 ± 0.0018	7,416 ± 39			
TP.M12-$C_{16:0}C_{18:0}$	1698.1.1	17670	Sp.420	183	0.4104 ± 0.0018	7,154 ± 35	-	No internal quality control	
TP.M24-$C_{16:0}$	1657.1.1	17617	Sp.420	102	0.4064 ± 0.0022	7,234 ± 46	-	Small C size, excluded	
TP.N02-$C_{16:0}$	1658.1.1	17809	B.103	96	0.4203 ± 0.0023	6,963 ± 47	X	Small C size, excluded	UCIAMS-113459
TP.N02-$C_{18:0}$	1658.1.2	17809	B.103	186	0.4035 ± 0.0020	7,292 ± 43		No internal quality control	
TP.N10-$C_{16:0}$	1699.1.1	17809	B.103	596	0.4021 ± 0.0014	7,318 ± 29	••	Included	
TP.N10-$C_{18:0}$	1699.1.2	17809	B.103	646	0.3991 ± 0.0014	7,378 ± 30			
TP.O23-$C_{16:0}$	1546.1.1	17630	B.72	175	0.4035 ± 0.0017	7,290 ± 36	••	Included	Poz-40796
TP.O23-$C_{18:0}$	1546.1.2	17630	B.72	439	0.3993 ± 0.0015	7,375 ± 32			
TP.O09-$C_{16:0}$	1656.1.1	17630	B.72	37	0.4132 ± 0.0032	7,099 ± 65	X	Small C size, excluded	
TP.O09-$C_{18:0}$	1656.1.2	17630	B.72	188	0.4061 ± 0.0021	7,239 ± 43		No internal quality control	
TP.O15-$C_{16:0}$	1655.1.1	15839	Sp.327	76	0.4003 ± 0.0024	7,354 ± 51	-	Small C size, excluded	Poz-40793/94
TP.P07-$C_{18:0}$	1701.1.2	13522	B.73	173	0.4065 ± 0.0017	7,230 ± 35	-	No internal quality control	UCIAMS-96507 UCIAMS-96510
TP.P13-$C_{16:0}$	1703.1.1	13522	B.73	312	0.4016 ± 0.0015	7,328 ± 31	••	Included	
TP.P13-$C_{18:0}$	1703.1.2	13522	B.73	615	0.3983 ± 0.0014	7,394 ± 29			
TP.P14-$C_{16:0}$	1591.1.1	13522	B.73	54	0.4173 ± 0.0034	7,021 ± 70	X	Small C size, excluded	
TP.P14-$C_{18:0}$	1591.1.2	13522	B.73	208	0.4045 ± 0.0020	7,271 ± 32		No internal quality control	
TP.Q05-$C_{16:0}$	1545.1.1	7841	Sp.414	60	0.4334 ± 0.0025	6,717 ± 55	•	Small C size, excluded	
TP.Q05-$C_{18:0}$	1545.1.2	7841	Sp.414	98	0.4337 ± 0.0022	6,712 ± 43		Small C size, excluded	
TP.Q06-$C_{18:0}$	1702.1.2	7841	Sp.414	241	0.4069 ± 0.0015	7,223 ± 32	-	No internal quality control	
TP.Q07-$C_{18:0}$	1700.1.2	7841	Sp.414	173	0.4146 ± 0.0017	7,072 ± 36	-	No internal quality control	
TP.R09-$C_{16:0}$	1592.1.1	7867	Sp.412	278	0.4177 ± 0.0019	7,012 ± 39	X	Non-identical within 2σ, excluded	UCIAMS-113460
TP.R09-$C_{18:0}$	1592.1.2	7867	Sp.412	759	0.4031 ± 0.0018	7,299 ± 38			

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ
X $C_{16:0}$ and $C_{18:0}$ dates non-identical within 2σ

4.4.3.3 Comparison with reference radiocarbon dates

This section focusses on the comparison of the uncalibrated CSRA dates to those included in the model, level-by-level. Four units of the dated sherds were already integrated in the model and the remainder came from other units than can be added within the stratigraphic sequence (Figure 4-8).

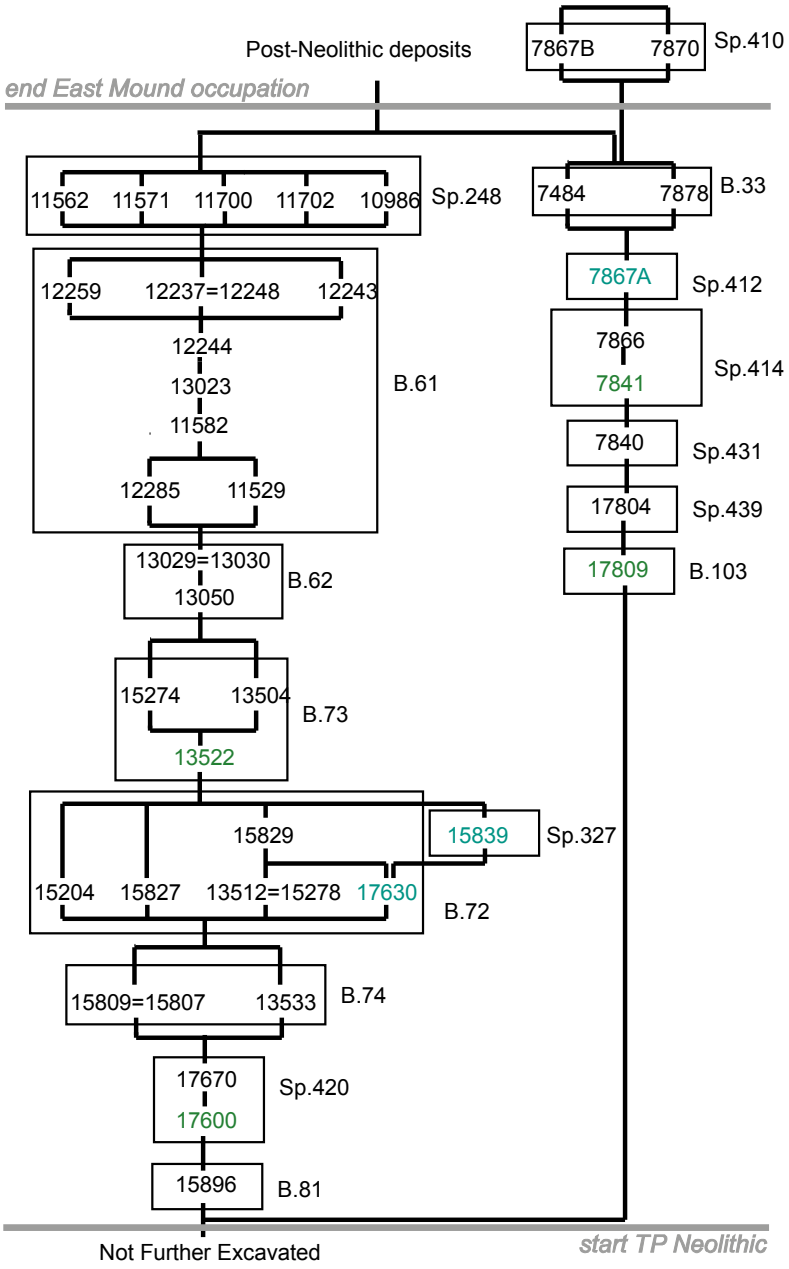

Figure 4-8: Schematic diagram showing the stratigraphic sequence used as a prior information in the chronological model. The unit in green correspond to those of the dated potsherds, in blue-green the ones already included in the model and in light green the ones added. Courtesy of A. Bayliss and M. Baranski.

4.4.3.3.1 Level M

Level M corresponds to one house B.81 and one feature Sp.420. The potsherds originate from context Sp.420 (Poz-40795: 7,380 ± 60 BP). Potsherd TP.M12 (dated by one target only to 7,154 ± 35 BP) exhibits younger ages than the reference dates, no internal quality control is available for this sherd. Potsherd TP.M17 shows statistically identical measurements on both FAs combined to 7,378 ± 27 BP, which correlated well to other dates from the feature Sp.420 (T' = 0.0, T'(5%) = 3.8, υ = 1). The dates on the potsherd TP.M24 were excluded due to low C yield.

4.4.3.3.2 Level N

The potsherds from level N originate from house B.103, which is not included in the modelled sequence. The dates which are included in the modelled sequence for level N are from either building B.74 (unusable dates from residual, intrusive or old wood samples) or from unit Sp.439 (UCIAMS-113459: 7,265 ± 60 BP). The dates for fatty acids from potsherd TP.N10 are combined to give a date of 7,348 ± 25 BP. The ^{14}C ages of the two potsherds TP.N02 (7,292 ± 43 BP, one target available) and TP.N10 are statistically consistent (T' = 1.4, T'(5%) = 3.8, υ = 1) but cannot be compared to the date included in the model as they do not come from the same context.

4.4.3.3.3 Level O

Level O consists of a house B.72 and features Sp.327 and Sp.431. Two potsherds came from the structure B.72 unit 17630, which was dated to 7,310 ± 50 BP (Poz-407696). Statistically consistent pairs of measurements were obtained for the fatty acids from TP.O23 (combined to 7,340 ± 27 BP) whereas potsherd TP.O9 (7,239 ± 43 BP) was only dated from one target. The

^{14}C dates from the lipids and the articulated bone successfully passed the χ^2 test at the 5 % level (T' = 6.8, T'(5%) = 9.5, υ = 3) for this stratigraphic feature. The potsherd TP.015 from the feature Sp.327 yielded insufficient C for reliable dating and comparison to the published dates.

4.4.3.3.4 Level P

Three potsherds were dated for this level from the unit number 13522 of house 73, with reference ^{14}C determinations coming from the same building, but not the same unit numbers. Potsherd TP.P07 exhibited a younger uncalibrated date than the reference dates. The dates from vessel TP.P13 (combined to 7,364 ± 25 BP), TP.P14 (7,271 ± 32 BP, one target), UCIAMS-96507 and UCIAMS-96510 passed the χ^2 test at the 5 % level (T' = 6.4, T'(5%) = 9.5, υ = 4). This result should be regarded with caution as the vessels were not from the same contexts as the reference dates.

4.4.3.3.5 Level Q

The Q level in the model corresponds to one building B.62 and two features Sp.414 and Sp.431. The 3 potsherds dated come the Sp.414 feature, however, the charcoal dates included in the dating program showed an old wood effect and cannot be used as reference. Of the three pottery vessels dated, one (TP.Q05) was excluded due to the low C yield and the other two, dated by only one target, are not consistent with one another (TP.Q06: 7,223 ± 32 BP and TP.Q07: 7,072 ± 36 BP). Overall, TP.Q07 looks too young for this level and could have been either contaminated during sample preparation or perhaps corresponds to an intrusive potsherd. The ^{14}C measurement on potsherd TP.Q06 seems consistent with the Q level dates, relative to the P and R level, but this cannot be further verified as no reference radiocarbon measurements are available for that phase.

4.4.3.3.6 Level R

The level R corresponds to the houses B.61, B.33 and feature Sp.412. The potsherd dated from R level, TP.R09, corresponds to one unit from Sp.412 dated to 7,130 ± 20 BP (UCIAMS-113460). However, the potsherd produced statistically inconsistent pair of measurements on the two fatty acids, and neither date on individual FA agrees with the reference, suggesting contamination of both FAs during the isolation procedure and compounds recovery.

4.4.3.4 Evaluation with Bayesian statistics

A total of 4 sherds whose measurements passed the internal quality control (and are thus regarded as accurate) were included and tested in the chronological sequence of the TP deposition (Marciniak *et al.* 2015). When the dates are integrated the model has an overall poor agreement (A_{model}: 53, not shown) and two dates TP.P13 (A: 16) and UCIAMS-96506 (A: 21) displayed poor individual agreements. Oddly, the posterior distribution of TP.P13 is constrained by the model as later than the radiocarbon date itself would suggest (Figure 4-9). In this model, the two refitted sherds have good individual agreement (TP.N10, A: 115; TP.O23, A: 140), which could indicate that the single sherd TP.P13 may have been residual in the context from which it was recovered.

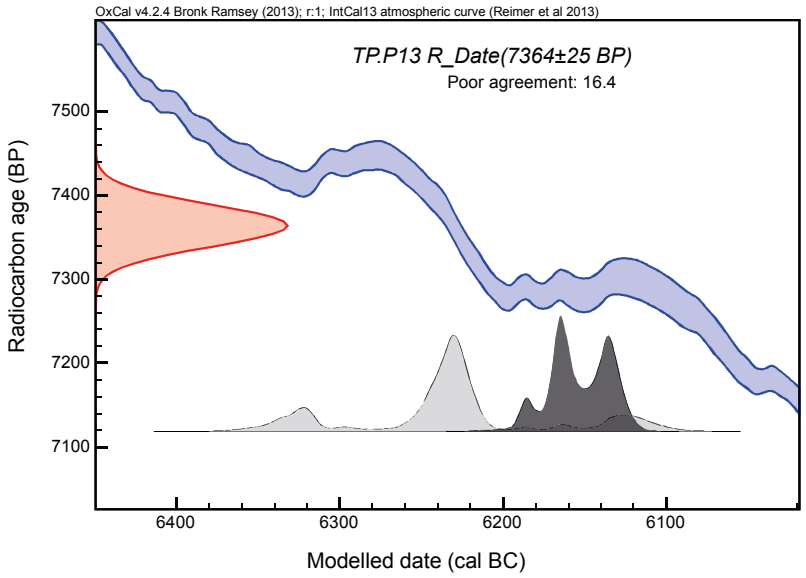

Figure 4-9: Probability distributions of radiocarbon date for potsherd TP.P13 in the initial model for Neolithic deposits in the TP area. The plotted distribution in light grey corresponds to the result of the simple radiocarbon calibration and plotted distribution in dark grey corresponds to the result of the calibration within the Bayesian statistical model. Courtesy of A. Bayliss (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

A revised model with this interpretation was run. The date on TP.P13 was included in unit 13522 as a *terminus post quem* date (i.e. 'limit after which'). The new model has an overall good agreement (A_{model}: 69; Figure 4-10) and the compound-specific dates on four pottery vessels show good individual agreements (TP.M17, A: 83; TP.N10, A:115; TP.O23, A:141; and TP.P13, A:112).

The new model presents an almost analogous posterior distribution for the key parameters in comparison to those of the original model. The median values vary by an average of 4 years and a maximum of 10 years (Appendix 4-4, 4-5; Marciniak *et al.* 2015, Figure 4).

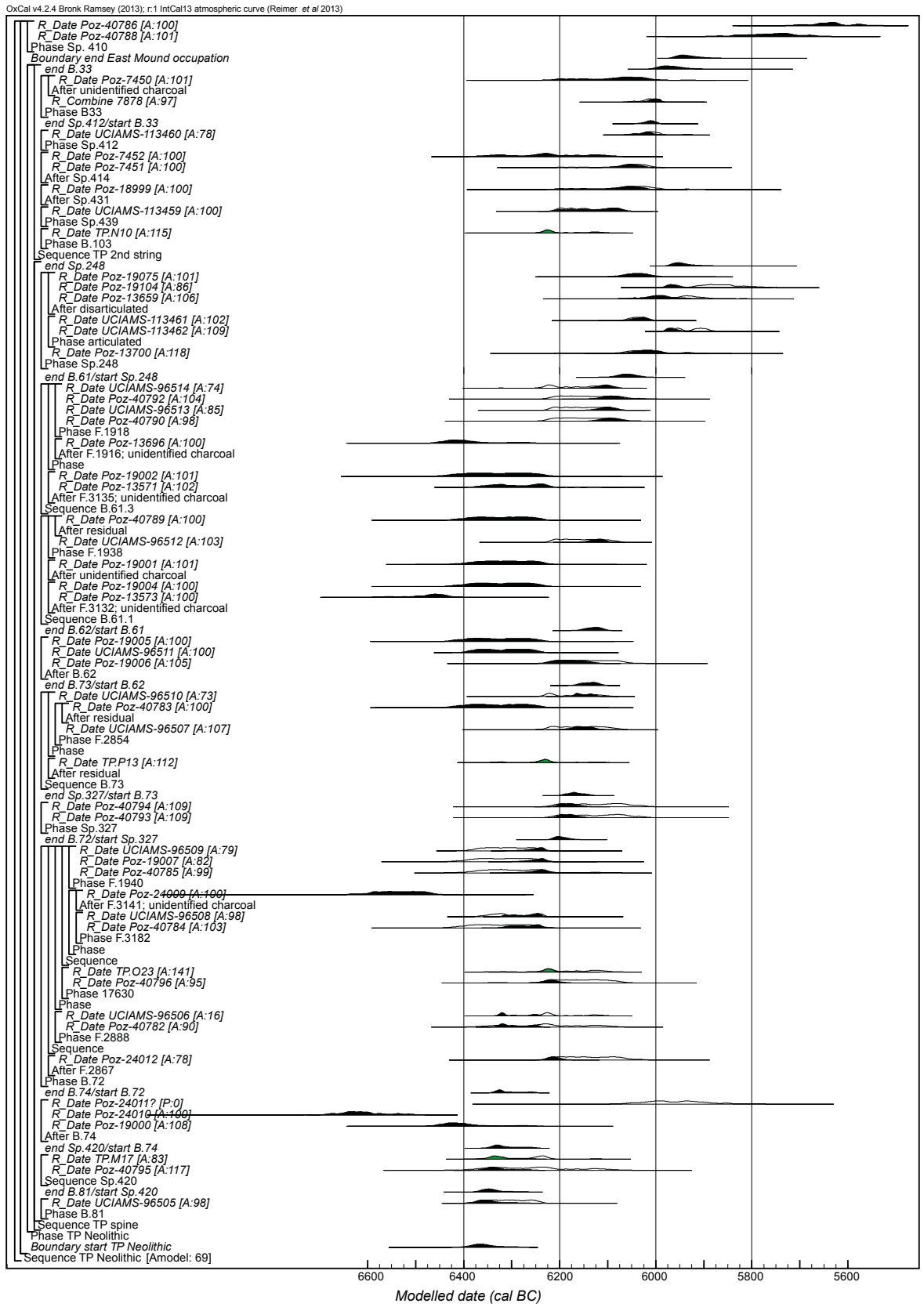

Figure 4-10: Probability distributions of radiocarbon dates from Neolithic deposits in the TP Area (including the results on absorbed fatty acids in pottery sherds listed). For each date, two distributions (representing the probability of an event to occur at a precise time) are displayed. The distribution in outline is the result of simple radiocarbon calibration, and the solid one is the result of the chronological model used. The distributions that are not linked to particular samples are output of the model, which is define by the square brackets on the left side and by the OxCal v4.2 keywords (Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013). Courtesy of A. Bayliss.

4.4.3.5 Discussion

The main issue with the CSRA dating of pottery at this site was the relatively low concentration of extracted lipids, and the small size of the available potsherds, which restricted sampling. This led to the generation of small C size targets that could not be reliably measured, highlighting that the lipid concentration in the potsherds is an essential parameter to consider when trying to obtain reliable dates. In addition, it appears that the uneven distribution of lipids preserved in the clay matrix may have resulted in an underestimation of the amount of sherd re-sampled (Charters *et al.* 1993b).

This study also showed that when two targets from one TLE are available, these do not necessarily pass the internal criterion (TP.R09). This potsherd failed the internal control on the two FAs despite the quality of procedural blanks during the extraction and processed standards for AMS (Sections 2.3.4.2, 2.4.7, 2.4.9). Another three potsherds (dated by only one target, TP.M12, TP.P7 and TP.Q7) exhibited younger ages than the references materials suggesting either contamination of the target (but the internal control is absent to verify such hypothesis) either intrusive single sherds in the context in which they are recovered. This suggests that target contamination is not constant and could likely occur at stages where one or two compounds could be contaminated unequally with exogenous C (e.g. PCGC isolation). Several hypotheses could explain this result: (i) graphite from the ferrules in the PFC contaminated one of the capillaries, (ii) the glass wool in the S-Trap got contaminated with exogenous C (e.g. dust) before fitting in the PFC or after its removal, (iii) the compound got contaminated during the transfer to tin capsule or (iv) one of the measurements corresponds simply to a statistical outlier. The cause was not determined clearly. However, by cross-contamination removal with the heat gun, two FAs isolated in individual traps would be unlikely contaminated by the same amount of exogenous C. Therefore, unless other evidence is available, age agreement between

the two FAs is considered in the rest of this thesis as evidence for the reliability of radiocarbon dates.

The remaining pottery vessels which generated enough C for a reliable dating showed good agreement with the reference dates. Among the sherds included in the Bayesian model one single sherd was probably reworked from an earlier context and is treated as a residual in the model, whereas the other sherds (including two refitting sherds) fitted well in the model. This could suggest that, where available, refitting sherds are preferred candidates for radiocarbon dating as this would avoid the selection of residual or intrusive potsherds. The revised model has an almost identical output to the original one. These CSRA from pottery vessels from Çatalhöyük correspond to the oldest dates on lipid extracts successfully produced in this thesis.

4.4.4 British Bronze Age pottery vessels from Cliffs End Farm

4.4.4.1 Site description

The site of Cliffs End Farm (CEF) is located on the Isle of Thanet (South East England; McKinley *et al.* 2014). The archaeological features (6 barrows and 3 enclosures) were occupied during the Bronze and Iron Age (Figure 4-11). The excavation revealed ca. 10,000 potsherds with a majority of sherds originating from the Late Bronze and Early Iron Age (McKinley *et al.* 2014). A dating program (104 dates) of archaeological material from the site targeted the Late Bronze Age features (Marshall *et al.* 2014). The duration of successive short deposits in pit 2028 was modelled by dating 15 pottery surface residues and 2 human bones, which showed good agreement (A_{model}: 74, Appendix 5-1, 5-2), making this a particularly suitable site for testing the dates obtained previously against both surface and adsorbed residues (from the same vessels) obtained using the new protocol. A total of 30 potsherds were submitted to ORA in the context of this thesis (Appendix 5-3).

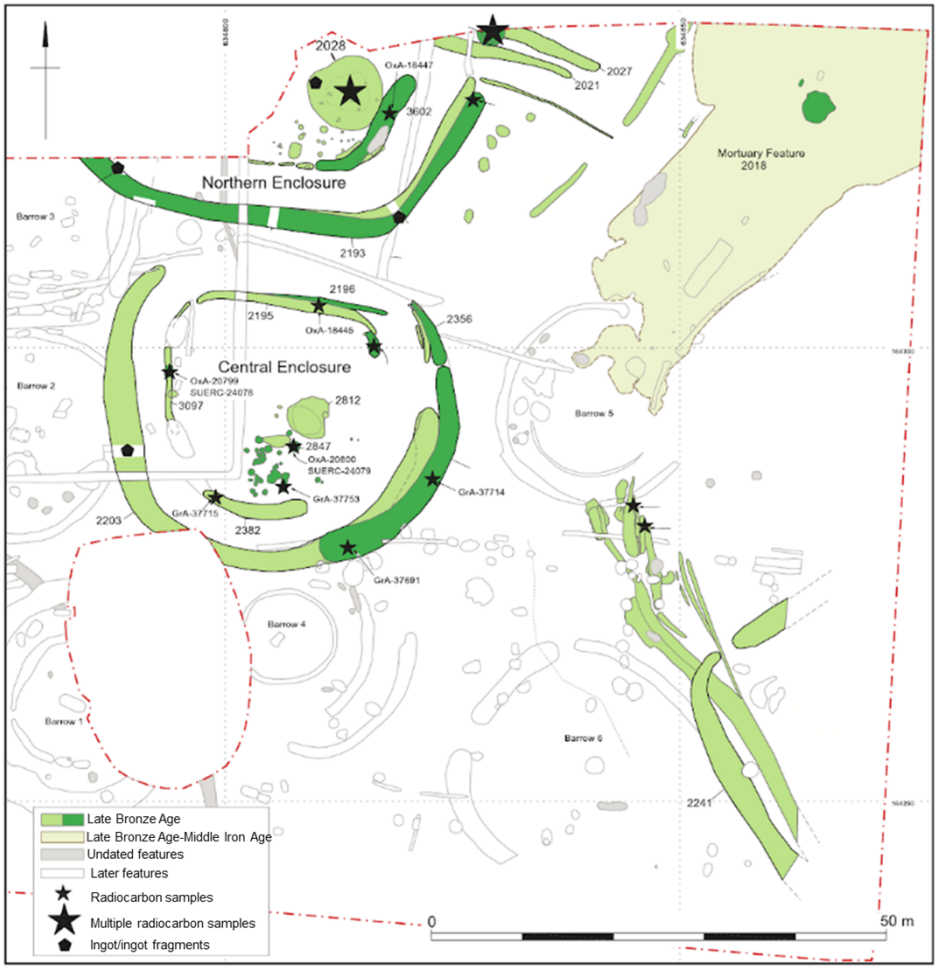

Figure 4-11: Map of the Cliffs End Farm site showing prehistoric features from Bronze Age and Iron Age including and the location of the archaeological materials dated. From Leivers and McKinley (2014, Figure 2.5).

4.4.4.2 CSRA determinations

A total of 4 pottery vessels from midden pit 2028, (layers 2, 5 and 8), dated from their surface residues, were selected for ^{14}C analysis (details in Appendix 5-4). The sherds CEF-C-6460, CEF-C-6468 and CEF-C-6470 from 3 different layers (2, 5 and 8 respectively) showed a statistically consistent pair of measurements for the radiocarbon dates of the $C_{16:0}$ and $C_{18:0}$ fatty acids (Table 4-6). Potsherd CEF-C-6471 required combining the $C_{16:0}$ and $C_{18:0}$ FAs to yield sufficient C for an AMS measurement. This combination was attempted as it has been discussed previously that C yields <100 µg could not be reliably measured, however, in such cases no internal quality control between the two FAs will be available.

Table 4-6: Compound-specific radiocarbon dates measured on fatty acids extracted from pottery from the pit 2028 at site of Cliffs End Farm.

Sample	BRAMS #	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range	Reference
CEF-C-6460-$C_{16:0}$	1956.1.1	299	0.7214 ± 0.0024	2,624 ± 28	••	OxA-17872
CEF-C-6460-$C_{18:0}$	1956.1.2	321	0.7261 ± 0.0024	2,572 ± 28		
CEF-C-6468-$C_{16:0}$	1955.1.1	470	0.6844 ± 0.0022	3,046 ± 27	•	GrA-35994
CEF-C-6468-$C_{18:0}$	1955.1.2	784	0.6864 ± 0.0021	3,023 ± 26		
CEF-C-6470-$C_{16:0}$	1954.1.1	168	0.6980 ± 0.0025	2,888 ± 30	•	OxA-17876
CEF-C-6470-$C_{18:0}$	1954.1.2	345	0.6966 ± 0.0023	2,904 ± 28		
CEF-C-6471-$C_{16:0}C_{18:0}$	1953.1.1	185	0.6706 ± 0.0024	3,210 ± 30	-	OxA-17988

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ

The $C_{16:0}$ and $C_{18:0}$ FAs from individual potsherds were combined to 2,598 ± 20 BP (T' = 1.7, T'(5%) = 3.8, υ = 1), to 3,034 ± 19 BP (T' = 0.4, T'(5%) = 3.8, υ = 1), to 2,896 ± 21 BP (T' = 0.2, T'(5%) = 3.8, υ = 1), for CEF-C-6460, CEF-C-6468, CEF-C-6470 respectively. Potsherd CEF-C-6471 was dated by one target (containing a mixture of the two FAs) to 3,210 ± 30 BP.

4.4.4.3 Comparison with reference radiocarbon dates

Upon comparison of the adsorbed lipids dates to the dates from the charred residues (previously dated) it was established that the CSRA dates of lipids displayed older values compared to surface residues (at 139, 275, 122 and 345 years for CEF-C-6460, CEF-C-6468, CEF-C-6470 and CEF-C-6471, respectively; Marshall *et al.* 2014). As the dates on both FAs successfully passed the internal quality control criterion on the two FAs, and the quality of procedural/processed blanks, it is unlikely that the difference between the visible residues and absorbed lipids can be attributed to an error made during the preparation of the absorbed FAs for ^{14}C dating (Section 4.4.3.5). Some older contamination during the pre-treatment, different for every potsherd, points at cross-contamination as exogenous C during the lipid extraction would have been detected by the procedural blank. The instrument and PFC were nonetheless, cleaned between every TLEs isolation. Therefore, remaining C in both capillaries that would

shift the CSRA determinations by the same amount of contamination for the two FAs and this occurring for every single TLE is unlikely. In this case, the agreement of both FAs dates can be considered as evidence for reliability on the CSRA dates despite their incompatibility with reference measurements.

4.4.4.4 Evaluation with Bayesian statistical model

When the CSRA dates are included, in the pre-existing Bayesian statistical model they push, back the start of the deposition to the 16th-15th century BC (A_{model}: 69; Figure 4-12). However, this pottery typology from the British Late Bronze Age is well-dated to the 10th - 9th millennium BC (Needham 2007; Best *et al.* 2012; Ladle and Woodward 2009). The earliest Late Bronze Age pottery assemblages do not appear before 12th -11th century BC in central and South West England (Figure 4-12; Best *et al.* 2012; Marshall *et al.* 2012). Thus, this shift to older ages is likely due to the 'old' radiocarbon age of CEF-C-6471, dated by a combination of $C_{16:0}$ and the $C_{18:0}$ FA (no internal quality control available) and its position in the model. When this sherd is excluded, the model has a good agreement (A_{model}: 69; not shown) and the start date of the pottery vessel in the midden pit is the 11th century BC, with a median value of 1,129 BC, which differs by only 15 years to the one produced by the original model (Appendix 5-3). Overall, the median values of the key parameters vary by an average of 14 years, with a maximum of 49 years, suggesting that the measurements are not accurate (despite their good agreement in the model) as the output is too different from the original model.

In this case, the dates compared correspond to the visible and adsorbed residues of the same potsherds. Therefore, any discrepancy between the adsorbed and surface residues dates (unlike the site of Çatalhöyük with potsherd TP.P13, Section 4.4.3.4) cannot be explained by the residuality of pottery vessels. The pottery FAs residues have an inbuilt quality control (passed

successfully), which contrasts with the surface residues which can only be evaluated against standards and other ^{14}C dates by a statistical testing or modelling. Although visible residues are prone to contamination with C from the burial environment leading to younger ages, both radiocarbon laboratories involved in the published dating program obtained good agreement on the dates. The discrepancy between the adsorbed and visible residues dates are therefore unlikely to result from pre-treatment issues.

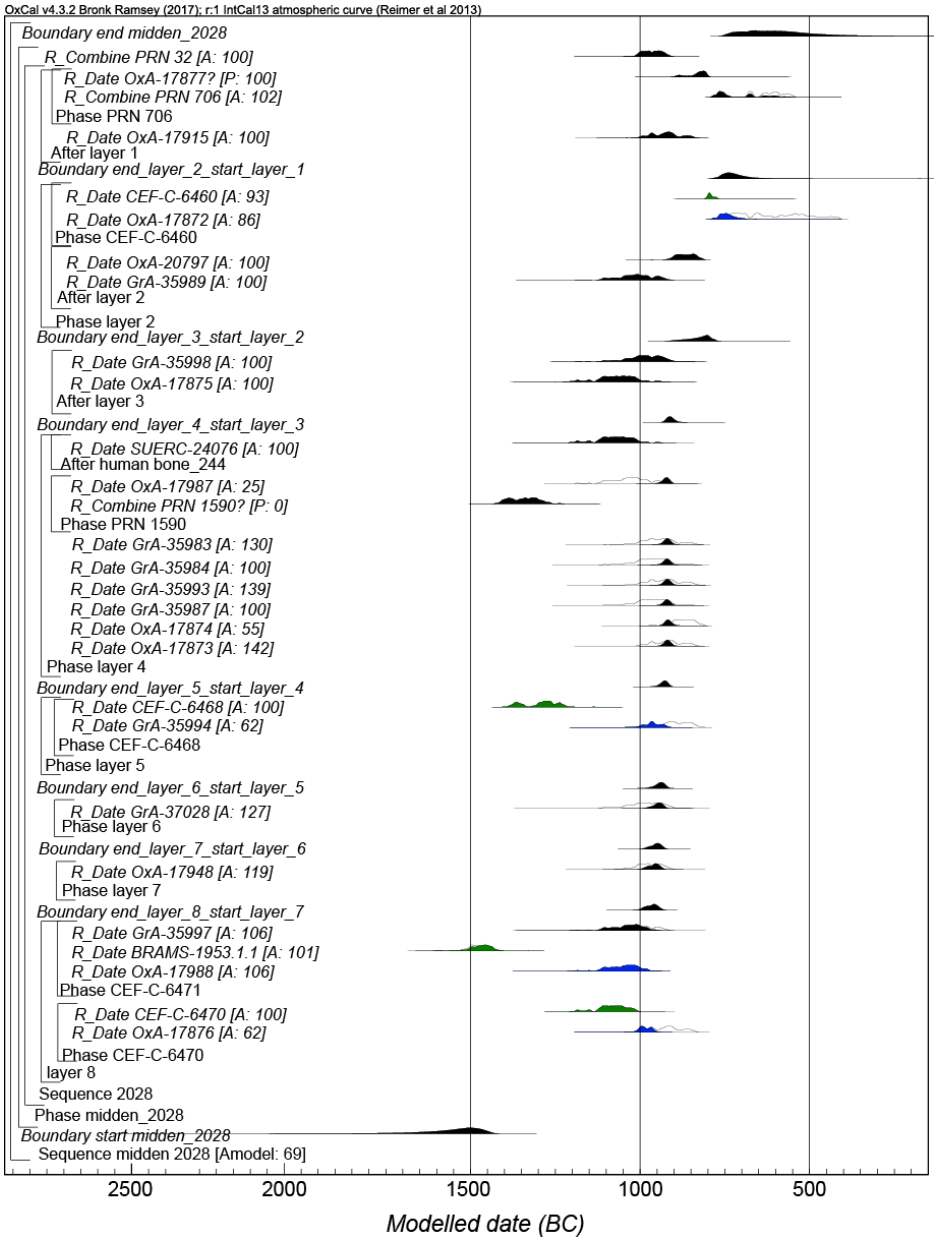

Figure 4-12: Probability distribution of all the dates used in the modelled sequence and of dates from lipids extracted from 4 pottery vessels. Format is as Figure 4-10, and the distributions plotted in blue those correspond to the dates on visible residues from the pottery dated by invisible residue. Courtesy of Professor A. Bayliss for the OxCal code (v4.2, Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013)).

However, it should also be noted that one surface residue (PRN1590) was dated 3 times in the publication giving 3 non-reproducible results between ca. 3,100 and 2,700 BP. This might suggest the marine reservoir phenomenon may be affecting the dates at the site and may therefore be the origin of the discrepancy between the published dates on surface residues and the new FA dates. The old wood effect phenomenon is excluded here as lipids were dated and these cannot originate from wood.

4.4.4.5 Influence of aquatic resources?

The site is located in a coastal area, however, no aquatic remains were excavated from pit 2028 or elsewhere at the site (McKinley *et al.* 2014). A total of 30 potsherds from the assemblage were analysed by ORA and twelve vessels presented lipid profiles characteristic of degraded animal fats (dominance of $C_{16:0}$ and $C_{18:0}$ FAs; Evershed *et al.* 1997, 2002a; Appendix 5-3). Therefore, SIM monitoring was undertaken in an effort to detect DYHAs or APAAs characteristic of aquatic resources. None of the potsherds contained long chain DHYAs. Two vessels (non-dated, CEF-C-6454, CEF-C-6469) did contain APAAs (C_{18}, C_{20} and C_{22}) with one (CEF-C-6454) presenting also the 4,8,12-trimethyltridecanoic acid (TMTD), suggesting some use of marine resources at the site (see Appendix 5-4). However, no aquatic biomarkers were detected in any of the dated sherds.

Furthermore, $\delta^{13}C$ values on the $C_{16:0}$ and $C_{18:0}$ FAs of the TLEs (n = 12) presenting animal fat residues were measured and are overall shifted along the mixing lines, between ruminant and non-ruminant adipose/marine products (Figure 4-13a; Section 1.1.2.3; Appendix 5-4). This shift from the reference ellipses of UK animals raised on a could suggest either the mixing between ruminant and non-ruminant products either the mixing between ruminant and marine products (Mukherjee *et al.* 2005; Cramp and Evershed 2014). In order to evaluate which

hypothesis is the most likely, the comparison of the $\delta^{13}C$ values of the TLEs with the faunal remains are necessary.

The faunal remains from the pit 2028 identified domesticated animals with a predominance of cattle, sheep and horse and with the pig bones corresponding to 1 to 4 % of the assemblage (Figure 4-13b; McKinley *et al.* 2014). The low frequency of pig bones in the assemblage, could support that they were not contributing significantly to the diet as opposed to the ruminant animals and thus not be at the origin of the enriched $\delta^{13}C$ values of the TLEs shifted from the reference ellipses of ruminant animals along the mixing lines.

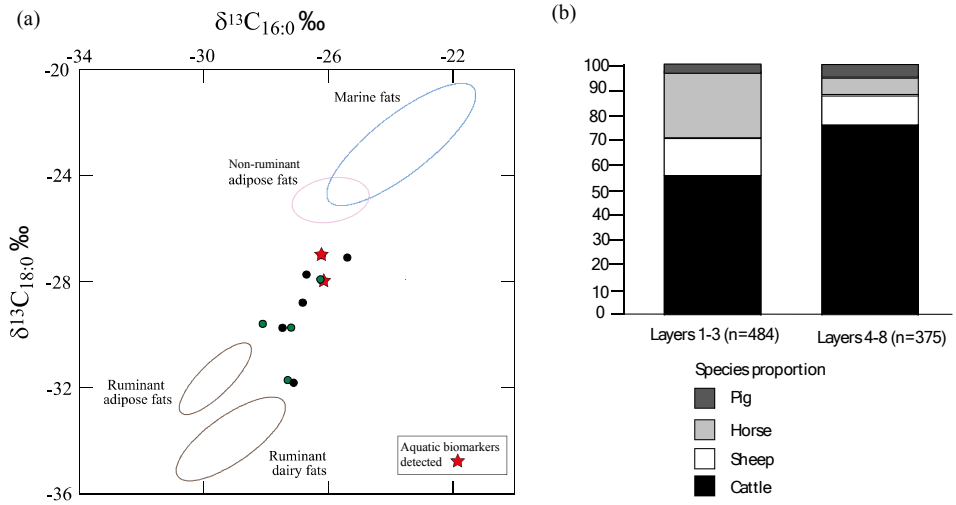

Figure 4-13: (a) Scatter plot of the $\delta^{13}C$ values for $C_{16:0}$ and $C_{18:0}$ fatty acids from animal products present within potsherds from Cliffs End Farm. Green dots correspond to the sherds dated, the black ones to the other potsherds analysed by ORA and stars the ones with aquatic biomarkers. Ellipses and ranges denote the values for modern reference fats from animals raised in pure C_3 diet and marine organisms (Copley *et al.* 2003; Cramp and Evershed 2014). (b) Faunal remains proportion in midden pit 2028 (from McKinley *et al.* 2014, Figure 5.8).

Although no fish remains were recovered from this pit, two lipid extracts suggest some use of marine products. It is then possible that the aquatic remains were missed during the excavation (Tauber 1981) or processed away from the site (Bird and Bliege Bird 1997). No aquatic biomarker was detected in the dated potsherds but, these biomarkers can be challenging to identify due to their survival in potsherds in low concentrations (Cramp and Evershed 2014). The age difference between the lipids and visible residues dated also increases with the

enriched carbon isotope values of the FAs (i.e. CEF-C-6460, closest to the reference ellipse of ruminant dairy, shows a difference of 139 y and CEF-C-6471, closest to the non-ruminant/marine product ellipse, shows a difference of 345 y). This could support that the TLEs with the most enriched $\delta^{13}C$ values contain the highest proportion of fish and thus present the most visible reservoir effect. Considering an average marine reservoir offset of 400 y (Harkness 1983) this age difference would correspond to ca. 35 % (CEF-C-6460), 69 % (CEF-C-6468), 31 % (CEF-C-6470) and 86 % (CEF-C-6471) of marine C in the potsherds. This result would be coherent with the $\delta^{13}C$ values in the case of no porcine carcass fats were processed in pots. Consequently, the discrepancy between CSRA and visible residue dates could be due to the mixing of terrestrial and aquatic products in the same vessel (see Chapter 7).

4.4.4.6 Summary

For the first time in all the examples investigated in this thesis, the CSRA results do not match the reference datable materials, being older than expected for a late Bronze Age pottery assemblage. However, all measurements of the FAs are consistent within 2σ for the individual sherds and, hence, it is unlikely that both compounds for all potsherds could be contaminated with the same amount of exogenous C excluding laboratory contamination. Old contamination from the archaeology could correspond either to old wood effect (but this is not possible as lipids were dated) or from a reservoir effect. While the faunal assemblage suggests only terrestrial animals were consumed, the detection of aquatic biomarkers in some of the pottery and the enriched carbon isotope values of the FAs, suggests that the discrepancy in the dates can be explained by a reservoir effect caused by the processing of aquatic resources in the pottery vessels. Interestingly, this case study emphasizes the fact that visible and adsorbed residues do not necessarily give the same dates, especially since, quite logically, they reflect different periods of the use life of vessels. Reservoir effects are discussed further in Chapter 7.

4.5 Conclusion

In this chapter the CSRA method developed in Chapter 3 was rigorously tested on archaeological bog butters and pottery vessels from well-dated archaeological contexts through comparisons with independently dated: (i) wood, dated via dendrochronology, (ii) radiocarbon measurements on bones collagen, including that from articulated bones, charcoal, grains and surface chars.

The CSRA dating of the archaeological pottery vessels has demonstrated the potential for wide application of the technique to dating pottery vessels of significantly different ages, recovered from diverse burial environments, significantly, achieving similar precisions to other commonly dated archaeological materials. The precision of ^{14}C measurements (obtained on a MICADAS instrument) on pot lipids were comparable or better than the date on reference materials (e.g. ca. 30-35 years precision on the ^{14}C dates from Cliffs End Farm on both reference and pot lipid dates, ca. 30-35 against ca. 50 years precision from Çatalhöyük). One advantage of dating two FAs from the same pot is to be able to combine the two measurements (Section 2.5.3.3) which improves the precision on the age of the potsherds to ca. 20-25 years, thus provides (in this Chapter) better precision than the reference ^{14}C measurements or indeed CSRA measurements from past studies (e.g. Eglinton *et al.* 1996; Stott *et al.* 2001).

Overall, the findings of these investigations have provided the basis for formulating a set of guidelines for the future use of the CSRA technique in routine archaeological dating:

(i) Given the widely varying lipid concentrations in pottery vessels and the homogeneity may exist in the lipid concentrations within vessels, potsherds possessing the highest concentration of lipids, i.e. >0.5 $mg.g^{-1}$ are the preferred targets for CSRA dating. Such

sherds can only be identified by ORA surveys of substantial numbers of sherds (30 to 50) representative of pottery assemblages.

(ii) Detailed analyses of lipid residues are essential in order to quantify and identify the sources of lipids prior to dating. Currently, degraded animal fats appear to be the best candidates, as these occur most frequently in archaeological pottery and in highest concentrations. Characterisation of sources through compound-specific carbon isotope analysis to identify fat type and GC-MS SIM to screen for aquatic biomarkers are vital to identify potential reservoir effects, introduced by the processing of marine or freshwater aquatic products in pots.

(iii) Dating of pottery based on the $C_{16:0}$ and $C_{18:0}$ FAs is the only dating method that offers two dates on the same sample. The ^{14}C dates on the two fatty acids should be the same allowing this to be exploited as a quality control criterion, i.e. if the dates for the $C_{16:0}$ and $C_{18:0}$ FAs do not agree within a 2σ error the dates on a sherd should be rejected as one or other, or both FAs have been contaminated. Re-analysis may correct this if the contamination has arisen through laboratory handling.

(iv) Where lower concentrations of FAs are recovered from a potsherd the $C_{16:0}$ and $C_{18:0}$ fatty acids can be combined (either by trapping into the same trap or by combining the contents of separate traps) to provide a single high precision date, however, under these circumstances the internal quality control comparison will be lost.

(v) The ^{14}C analysis of FAs from extracts which show evidence of aquatic contributions and thus reservoir effect has potential to be corrected. This will be explored further in Chapter 7 of this thesis.

Chapter 5.

From lipid residue analysis to CSRA of pottery vessels in Neolithic Alsace

Chapter 5. From lipid residue analysis to CSRA of pottery vessels in Neolithic Alsace

5.1 Potsherds selection for ^{14}C dating

Radiocarbon dating programs are established to answer archaeological questions and require a rigorous selection of the materials to be dated, including pottery vessels. Building chronologies using a Bayesian statistical modelling method requires a clear definition of archaeological information from the relevant site and an understanding of the archaeological questions to be addressed (Bayliss and Bronk Ramsey 2004). This understanding of the site archaeology, particularly of the relative chronology and taphonomy, greatly influences the selection of samples as residual, intrusive or long-lived materials should be avoided (Bayliss *et al.* 2011). In Chapter 4, it was shown that potsherds with high lipid concentrations are good candidates and can be reliably dated if residual sherds, or the ones affected by a reservoir effect, are avoided. The question still arises of how best to select sherds from a pottery assemblage with the aim of carrying out a radiocarbon dating program and how many vessels from an assemblage will be suitable for dating?

5.1.1 Sampling strategies for lipid residue analysis

Prior to any dating, a pre-screening with conventional ORA of a pottery assemblage is required to determine which sherds comprise lipid compositions and concentrations suitable for dating. Previously, sampling strategies for ORA were established, based on studies performed by Charters *et al.* (1993b), which showed the preferential absorption of lipids in the upper parts of cooking vessels, with concentrations becoming progressively less down the vessel profile. Different vessel types could present different lipid concentrations and distributions, due to

vessel specialisation for certain commodities or activities (e.g. Charters *et al.* 1995; Salque *et al.* 2013). Vessel specialisation could influence potsherds selection as only potsherds with animal products are targeted due to their high recovery and lipid concentrations, as opposed to those with lipid profiles characteristic of beeswax or plant. Additionally, potsherds with products from a ruminant animal which feed on grass only (one source of C) are better candidates than potsherds with products from omnivores animals which can feed on several products including marine products (several sources of C). Thus, vessel specialisation could determine the suitability of potsherds for ^{14}C dating based on lipid concentrations and animal fats origin. For ORA, ca. 30 potsherds, from the upper part of the vessels, per variable (phase, pottery shape, decoration etc) are needed to obtain statistically representative results but the selection of the sherds is, of course, dependent on the research question. To date, based on the results detailed in previous chapters, a requirement of the potsherds for ^{14}C dating is a sherd size which allows the sampling of up to 7 g (~2 g for ORA and up to 5 g for ^{14}C dating) of vessel fabric.

5.1.2 Reflection on sampling strategies for ^{14}C dating

Another constraint on the sherd selection will come from knowledge of the archaeology at the site. In radiocarbon dating, sample types are required to meet three main criteria: (i) be in equilibrium with the atmosphere during its lifetime, (ii) not be contaminated by other materials containing carbon, and (iii) be securely associated with the event to be dated (Bayliss *et al.* 2011). Therefore, only short-lived materials (which is the case for lipid residues) from closed depositional contexts are selected. Common sampling strategies to avoid residual or intrusive materials in such closed contexts select, for instance, (from the most to least favourable): (i) articulated bones connected with soft tissues, (ii) bones recognised as articulated, (iii) bones with refitted unfused epiphyses, (iv) carbonised food residues on refitted pottery sherds from

closed contexts, (v) antler tools, (vi) short lived waterlogged wood, (vii) charred plant remains related to the context of discovery, (viii) pairs of bones judged to be from the same animal, (ix) groups of bones deliberately deposited together, (x) fragile charred plant remains, (xi) carbonised food residues on single sherds, and (xii) well-preserved disarticulated bones (Bayliss *et al.* 2011). Similar strategies to select pottery vessels from a closed context to avoid residual materials would be (from the most to least favourable): (i) refitted sherds, (ii) sherds judged to be from the same pottery vessel, (iii) single decorated sherds which decorative motifs fit in a seriation study, (iv) single undecorated sherds deposited alongside decorated sherds with decoration fitting in a seriation study, (v) single undecorated sherds. All the above parameters must be taken into account to allow optimum sampling of the pottery assemblage This is particularly important if the dates generated are to be included in a modelling program. However, there could be a discrepancy between the (known) ideal pottery vessels to be dated and those sherds (from a site) that actually would be datable (i.e. a high lipid concentration with the potential to obtain ca. 200 μg of C from both FAs, with no contribution from aquatic resources).

5.2 Aims and objectives

The aim of this chapter is to perform ORA of vessels from the well-dated Alsace region (Section 5.3) as a test of the use of CSRA of pottery. Firstly, lipid residue analyses were carried out on pottery assemblages from the Early Neolithic in the Lower and Upper Alsace regions and sites from the Middle Neolithic in the Lower Alsace. The aim of these analyses is to reconstruct diet and subsistence practices in the region based on ORA and complementary faunal remains. This would allow detecting datable potsherds based on their lipid profiles and to detect/rule out any use of products from an aquatic reservoir that could affect ^{14}C dates. This will also allow optimal sampling strategies for future radiocarbon dating programs to be

established. The second objective is to CSRA date a selection of pottery vessels from the Lower Alsace region and integrate the dates in the pre-existing regional models (Denaire *et al.* 2017). The regional models were built using the sequence of LBK and Middle Neolithic ceramic assemblages, which will allow the direct comparison of radiocarbon dates on pottery vessels to the relative pottery chronology established by seriation and typological analyses. This will provide a test of the CSRA method at a regional rather than a site scale.

5.3 The domain of study: The Neolithic Alsace

5.3.1 The early Neolithic and LBK culture

The Early Neolithic in the Alsace region (France) comprises more than 140 sites from the *Linearbankeramik* or linear pottery culture (LBK), whose name originates from its ceramic assemblage presenting characteristic decoration with curved lines. The LBK culture settled in an area of approximatively 750,000 km^2, preferentially on loess soil and in proximity to rivers (Bogucki 2000). The earliest LBK settlements were located in central Europe in the Danubian Basin ca. 54th century BC (Bogucki 2000; Jakucs *et al.* 2016). The culture spread East to the Carpathians, north to the Kujavia and Pyrzyce regions in Poland and West to the Neckar Valley, Rhine Valley and Parisian Basin (Bogucki 2000; Price *et al.* 2001; Marciniak 2008; Figure 5-1). The LBK people uniformly settled in open-air sites in long rectangular or trapezoidal houses (up to 45 m long; Bogucki 1995). The culture corresponds to the first farming group in central Europe. They raised animals with cattle dominating over sheep, goats and pigs with hunting being a relatively minor part in their economy (Bogucki 2000).

Five main phases have been recognised for this culture: Earliest LBK, Early LBK, Middle LBK, Late LBK and Final LBK. These can also be subdivided depending on the duration of settlements in different regions (Meier-Arendt 1966). Even though the culture showed overall

similarities, especially for the earliest LBK settlements, regional differentiation in pottery style, settlement and/or funerary practices later emerged (Bogucki 2000).

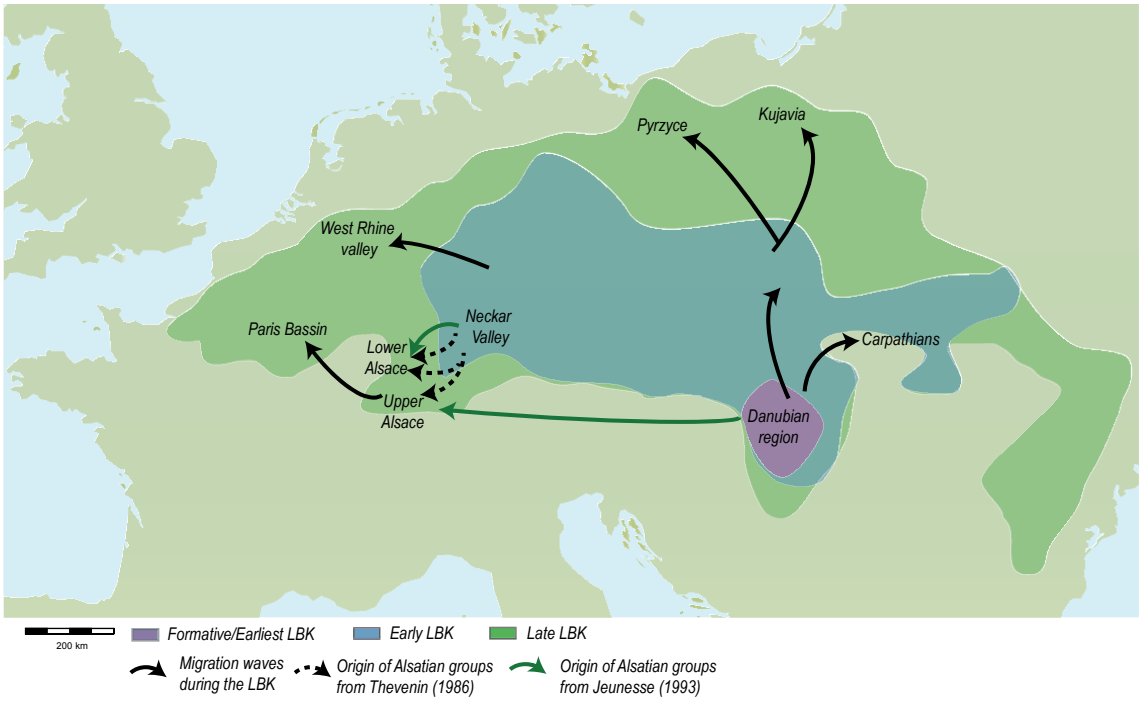

Figure 5-1: Spatial repartition of LBK groups in Europe from Earliest to Late LBK with the main waves of migration including the two hypothesis or origins of Alsatian groups.

In Alsace, LBK sites can be divided into two distinct cultural groups: those from Lower Alsace (LA, northern groups) and those from Upper Alsace (UA, southern groups). The examination of sites from both Lower and Upper Alsace shows they appear to have different cultural tradition as regards to funerary practice, architecture and pottery style (Jeunesse 1995; Lefranc 2007). It was also reported that domesticated animal assemblages were dominated by cattle with pigs as secondary animals in the LA and small ruminants like sheep/goat as secondary animals in the UA suggesting also different herd management. The hypothesis of two different origins for these geographically close settlements has therefore been put forward. The origins of both groups are quite complex and are believed to be either from the Neckar Valley (Thévenin 1986) for both groups, or, from the Neckar valley for LA and the Danuban region for UA (Figure 5-1). Whereas the LA group did not extend further, the UA group migrated to

the Parisian Basin during the Middle LBK (Lefranc 2007). In spite of their different identities, Alsatian groups are known to have interacted, probably because of their geographical closeness. The sites Wettolsheim, "Ricoh" or Colmar, "Route de Rouffach" have shown mixed ceramic assemblages from Lower- and Upper-Alsace from the Early LBK and are considered to be border sites (Lefranc 2007).

The different cultural groups of the two Alsatian groups were highlighted through vessel seriation (Jeunesse 1993a, 1995, Lefranc 2007). This study also showed temporal differences between the stylistic pottery evolution in the two regions (Figure 5-2).

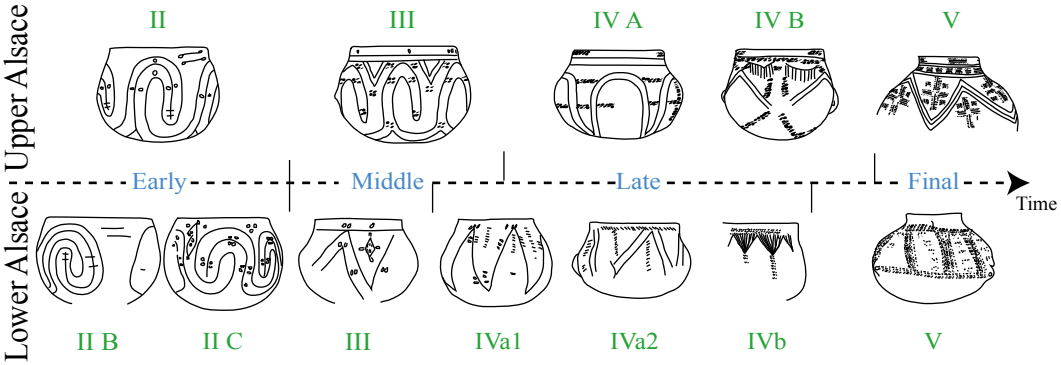

Figure 5-2: Pottery with decorative motifs representative of successive LBK phases of the regional groups in Alsace and relative chronology. Adapted from Lefranc (2007).

5.3.2 The Middle Neolithic

Following the LBK is the Middle Neolithic, which comprised a succession of cultures defined by their pottery style, although their cattle-based economies followed the LBK tradition (Jeunesse 1991; Bogucki 2000). The cultures succeeding the LBK in Alsace were, in chronological order, Hinkelstein, Grossgartach, Planig-Friedberg, Roessen, Bischheim, Bruebach-Oberbergen and *Bischheim Occidental du Rhin Supérieur* (BORS; Figure 5-3). The Alsace was therefore intensively and continuously occupied until the arrival of the Michelsberg culture in the region ca. 4,200 BC, which marked the end of the Middle Neolithic (Denaire *et*

al. 2017). Numerous sites of such cultures were also recovered outside of the Alsace in the Neckar, Wetterau, Baden, Lake Constance, Moselle Valley or central Germany region demonstrating their settling of a vast area (Denaire 2009b).

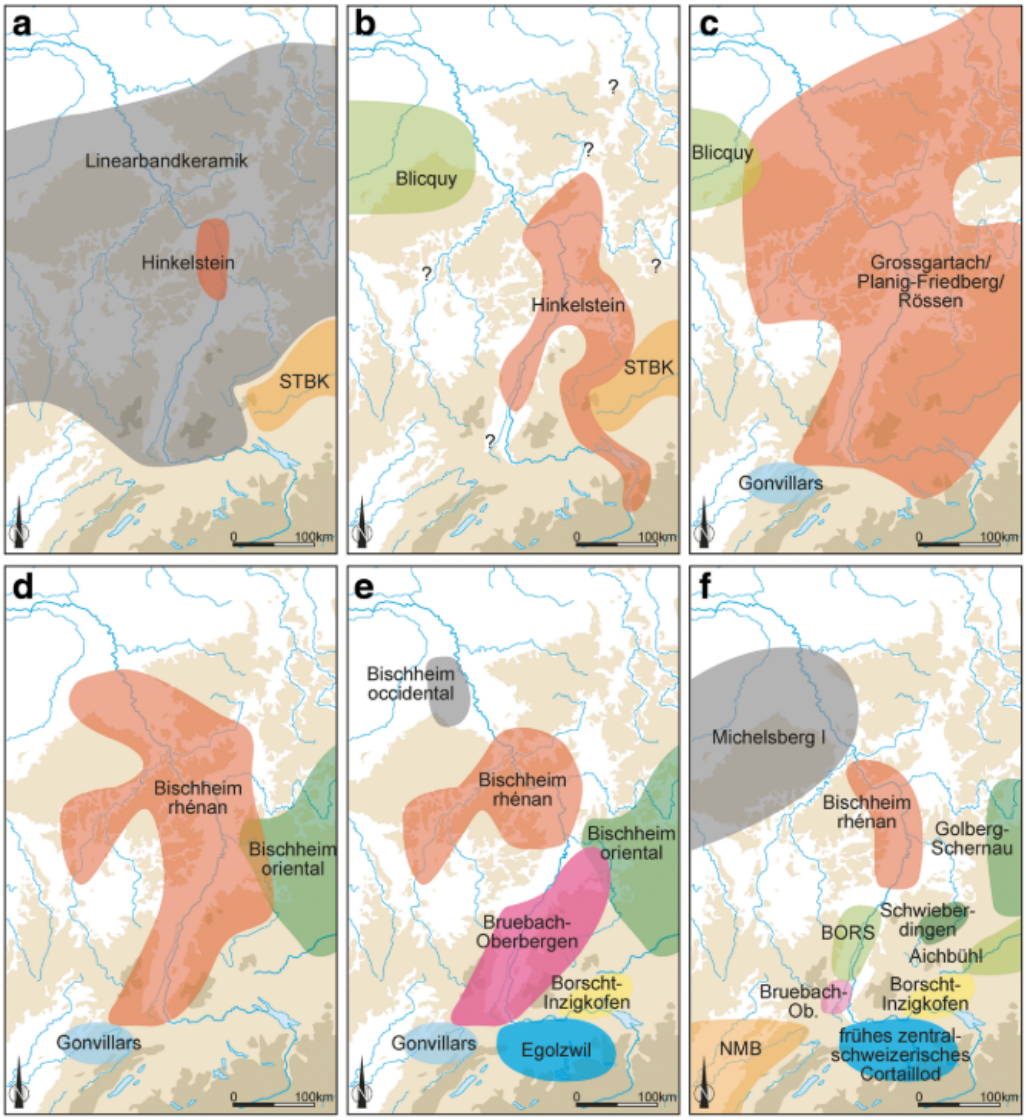

Figure 5-3: Map of the Rhine valley and surrounding areas with occupation during the Neolithic of (a) LBK, (b) Hinkelstein, (c) Grossgartach, Planig-Friedberg, Roessen (d) Bischeim, (e) Bruebach-Oberbergen and (f) BORS. From Denaire *et al.* (2017, Figure 3).

The first Middle Neolithic culture in Alsace inhabited the same areas of the LBK (Jeunesse 1993a; Denaire 2009a). The transition between the LBK and Hinkelstein in LA is poorly understood and, for a long time they, were thought to coexist (Denaire 2009a), but radiocarbon dating of animal bones from both cultures determined that the final LBK and early Hinkelstein

cultures are not contemporaneous (see Section 5.3.3; Denaire *et al.* 2017). Population size decreased from the Late LBK to the Hinkelstein culture, remaining stable until the first phase of the Grossgartach and an increase in the number of settlements with later phases (Denaire 2009a). Pottery vessels, finery and funerary practices suggested the genetical link of the Middle Neolithic groups (Denaire 2009b). Work on pottery seriation performed by Denaire (2009a) showed linked decoration motifs for Hinkelstein, Grossgartach, Planning-Friedberg and Roessen groups with the additional distinction of 5 phases during the Grossgartach.

5.3.3 Radiocarbon dating of the Lower Alsace

After intermittent radiocarbon dating of sites in the region (Denaire 2009b, 2011) the Lower Alsace region was the subject of an extensive dating program, from articulated bones and visible residues associated with pottery vessels (Denaire *et al.* 2017). The new program involved the application of a mathematical model, using Bayesian statistics, both to understand the Neolithic occupation of the region and also test the validity of the relative ages of the period, determined via the seriation studies. The model was built using radiocarbon determinations, together with pottery seriation, which was used as prior information on the relative ages of the different contexts. Special care was taken to select short-lived materials from closed contexts (articulated bones, n = 57; articulating bones, n = 29; animal bone with refitting unfused epiphyses, n = 19; paired bones judged to be from the same animal, n = 4; visible residues on pottery vessels, n = 6) of the Early and Middle Neolithic groups (Denaire *et al.* 2017). Dates from three tree-rings and radiocarbon measurements on charcoal, grain and pitch from previous studies were also included.

The seriation study covered 112 LBK assemblages, with 87 decorative motifs, from 20 settlements. The correspondence analysis allowed the separation of 7 phases which

corresponds to the temporal sequence (Appendix 6-1). A total of 56 radiocarbon measurements obtained from 48 archaeological materials from all ceramic phases, except phase V (no datable materials), were included in the Bayesian statistical model. The model shows good overall agreement (A_{model}: 61; Bronk Ramsey 2009; Appendix 6-2) although 3 measurements were excluded from the analysis and a further two were interpreted as residual. The results of the chronology (Denaire *et al.* 2017) showed the appearance of LBK groups in the region 5,355 – 5,240 cal BC (95 % probability) with occupation ending between 5,145 – 5,020 cal BC (95 % probability; Figure 5-4).

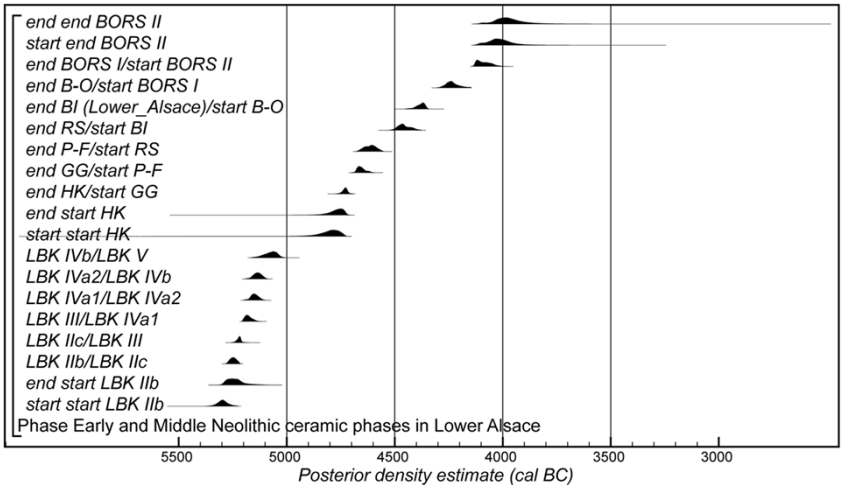

Figure 5-4: Phase boundaries derived from the Bayesian statistical models for the chronology of the Early and Middle Neolithic in the Lower Rhine region. From Denaire *et al.* (2017, Figure 21).

In addition, 190 pottery assemblages with 208 decorative motifs from 27 Middle Neolithic settlements (Hinkelstein to Roessen groups) were divided into 4 phases by correspondence analysis (Appendix 6-1; Denaire *et al.* 2017). Furthermore, this revised seriation study allowed the recognition of 5 sub-phases of the Grossgartach group but not as clearly as the original seriation by Denaire (2009a). For the following groups, the Bischheim and Bruebach-Oberbergen, showed uniformity in their decoration motif precluding any seriation study and the BORS culture was divided, into 3 subphases, using correspondence analysis based on 42 assemblages and 41 decorative motifs from 11 settlements (Denaire *et al.* 2017). A total of

95 radiocarbon measurements from 84 archaeological materials from assemblages of the Middle Neolithic groups were combined with the sequence of ceramic phases in the Bayesian statistical model. The model showed an overall good agreement (A_{model}: 100; Bronk Ramsey 2009; Appendix 6-2). A break in occupation between the LBK and Hinkelstein cultural groups was revealed, with the earliest settlement of the Hinkelstein starting 4,910 – 4,725 cal BC (95 % probability; Figure 5-4). No such discontinuity was visible for the succession of the following groups. The transition from Hinkelstein to the Grossgartach occurred 4,765 – 4,705 cal BC (95 % probability), followed by transition to Planig-Friedberg at 4,690 – 4,610 cal BC (95 % probability) and then to the Roessen culture at 4,670 – 4,565 cal BC (95 % probability). Furthermore, the model rejected the 5 sub-phases determined by seriation on the Grossgartach assemblages suggesting the contemporaneity of decoration of pottery vessel styles rather than a chronological succession. The later groups began with the Bischheim culture 4,515 – 4,395 cal BC (95 % probability) and ended with the BORS 4,115 – 3,805 cal BC (95 % probability; Denaire *et al.* 2017).

This study shed new light on the occupation of the region by prehistoric farmers and serves as a reference for the CSRA of pottery assemblage. To date, no equivalent dating program has been performed in the Upper Alsace.

5.4 Lipid residue analysis of Neolithic sites from the Alsace region

Pottery assemblages were carefully selected for this regional study (Figure 5-5). These consist of sites containing LBK material from the Early to the Final phase of the LBK in both LA and UA and also include one site on the border between the two regions, which comprised pottery from both regional traditions. In addition, one Middle Neolithic site from the LA with Grossgartach and Roessen pottery was selected.

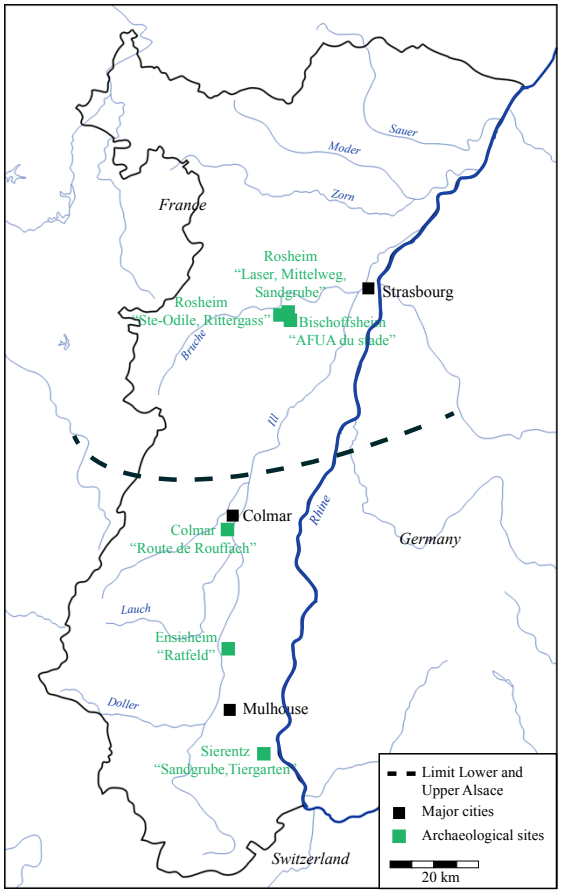

Figure 5-5: Map of the Alsace region showing the boundary between the Lower and Upper Alsace and the sites selected for ORA.

The pottery vessels were selected, when possible, from the upper part of the vessel to maximise the lipid recovery and mainly came from closed contexts (i.e. not disturbed, with decorated pottery vessels of one LBK phase only) relatively dated by seriation analysis. A total of 390 potsherds, comprising 51 refitted sherds and 174 decorated vessels, were sampled for the LBK in the LA region. A total of 395 potsherds, including 41 refitted sherds and 127 decorated sherds, were selected for the LBK from the UA region. Finally, 86 potsherds, with 26 refitted sherds and 21 decorated vessels, were sampled from the Middle Neolithic groups in LA. The bias in sampling reflects the occurrence of refitted sherds in the assemblages (Appendix 6). ORA are necessary to identify sherds suitable for dating. As the Alsace region is a considerable distance from the coast, a marine contribution is highly unlikely. But the processing of freshwater organisms (Cramp and Evershed 2014) is an important consideration as most of the

Neolithic settlements in Alsace are in proximity to river or streams and thus could influence radiocarbon dates.

5.4.1 Lipid residue analysis of Early Neolithic sites from the Lower Alsace

5.4.1.1 Sites description

Two LBK sites, with material integrated into the regional dating program, were sampled. The site of Bischoffsheim (BIS), located in the Lower Alsace, 25 km from the city of Strasbourg comprised up to 41 LBK houses with overlapping structures (Jeunesse and Sainty 1991; Lefranc *et al.* 2004; Appendix 6-3). The site showed a long occupation settlement with 6 phases of occupation from the Early LBK IIB to the Late LBK IVb (Lefranc *et al.* 2004).

The city of Rosheim (ROS), located 2 km from the site of Bischoffsheim, was excavated in 1989 ("Sainte-Odile"; Jeunesse and Lefranc 1999) and 2012 ("Rittergass"; Lefranc and Michler 2015) and revealed occupation levels dating to the Early Neolithic, Late Neolithic and Iron Age (Appendix 6-4). The LBK occupation during the Early Neolithic included three houses assigned to the Late LBK IVa and IVb as well as one enclosure ditch (Jeunesse and Lefranc 1999; Lefranc 2007; Lefranc and Michler 2015). The enclosure ditch showed different sections ascribable to the Late and Final phases and thus was likely used for several generations.

5.4.1.2 GC and GC-MS analyses

A total of 290 potsherds from Bischoffsheim and 103 potsherds from Rosheim were analysed (Sections 2.3.2, 2.4.1, 2.4.2; Appendix 6-5 and 6-6). Total lipid extract concentrations ranged from > 5 $\mu g.g^{-1}$ from 79 % (n = 229) of the potsherds from Bischoffsheim and from 72 % (n = 74) of the potsherds from Rosheim were recovered. These had an average lipid

concentration of 213 $\mu g.g^{-1}$ and 403 $\mu g.g^{-1}$, respectively. A total of 11 potsherds from Bischoffsheim and four from Rosheim showed high lipid concentrations above 1 $mg.g^{-1}$ of sherd (e.g. BIS-C-4063: 6.5 $mg.g^{-1}$; BIS-C-4518: 4.3 $mg.g^{-1}$; ROS-C-2201: 3.3 $mg.g^{-1}$; ROS-C-4678: 4.6 $mg.g^{-1}$) demonstrating a good preservation of lipids.

A total of 30 % (n = 67) for Bischoffsheim and 46 % (n = 34) for Rosheim of the TLEs were dominated by $C_{16:0}$ and $C_{18:0}$ FAs, characteristic of degraded animal fats (Figure 5-6). The odd-numbered $C_{17:0}$ FA, and *iso*- and *anteiso*-isomers, possibly indicative of microbial activity in the rumen and thus characteristic of a ruminant product origin, were also present (ca. 40 potsherds; Keeney *et al.* 1962). These FAs distributions were mainly recovered from undecorated vessels. In two potsherds (BIS-C-4568 and BIS-C-5324) the presence of odd-carbon numbered ketones (31 to 35), formed by pyrolysis of FAs via ketonic decarboxylation, indicative of heating to high temperatures (>300 ºC, see Evershed *et al.* 1995; Raven *et al.* 1997) were recovered.

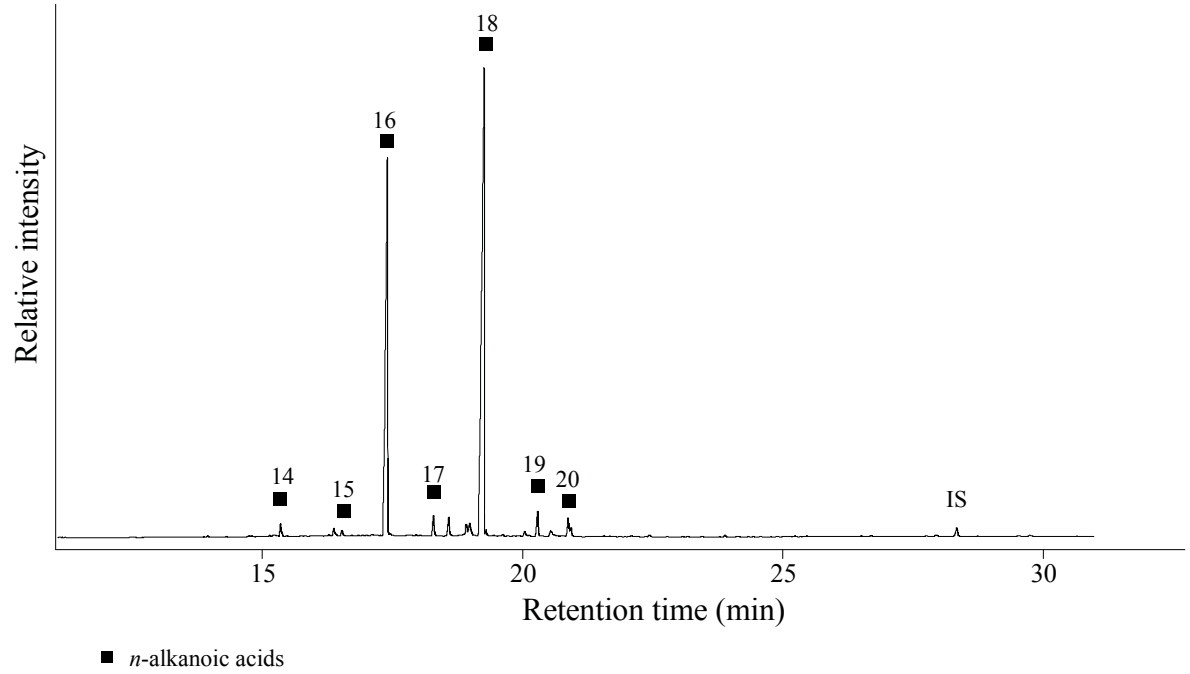

Figure 5-6: Partial gas chromatogram of the potsherd BIS-C-4519 showing lipids distribution ascribable to terrestrial animal fats. IS is the internal standard, the numbers correspond to the carbon chain length of the biomarkers.

The lipid profile of a number of the sherds, 17 % (n = 39) from Bischoffsheim and 16 % (n = 12) from Rosheim included even-carbon numbered n-alcohols (C_{24} to C_{32}), odd-carbon numbered n-alkanes (C_{23} to C_{33} maximizing at C_{27}) and even-numbered FAs ($C_{16:0}$ then C_{24} to C_{36}) that are characteristic of hydrolysed beeswax (Regert *et al.* 2001; Correa-Ascencio and Evershed 2014; Figure 5-7; e.g. BIS-C-4034 and ROS-C-2144).

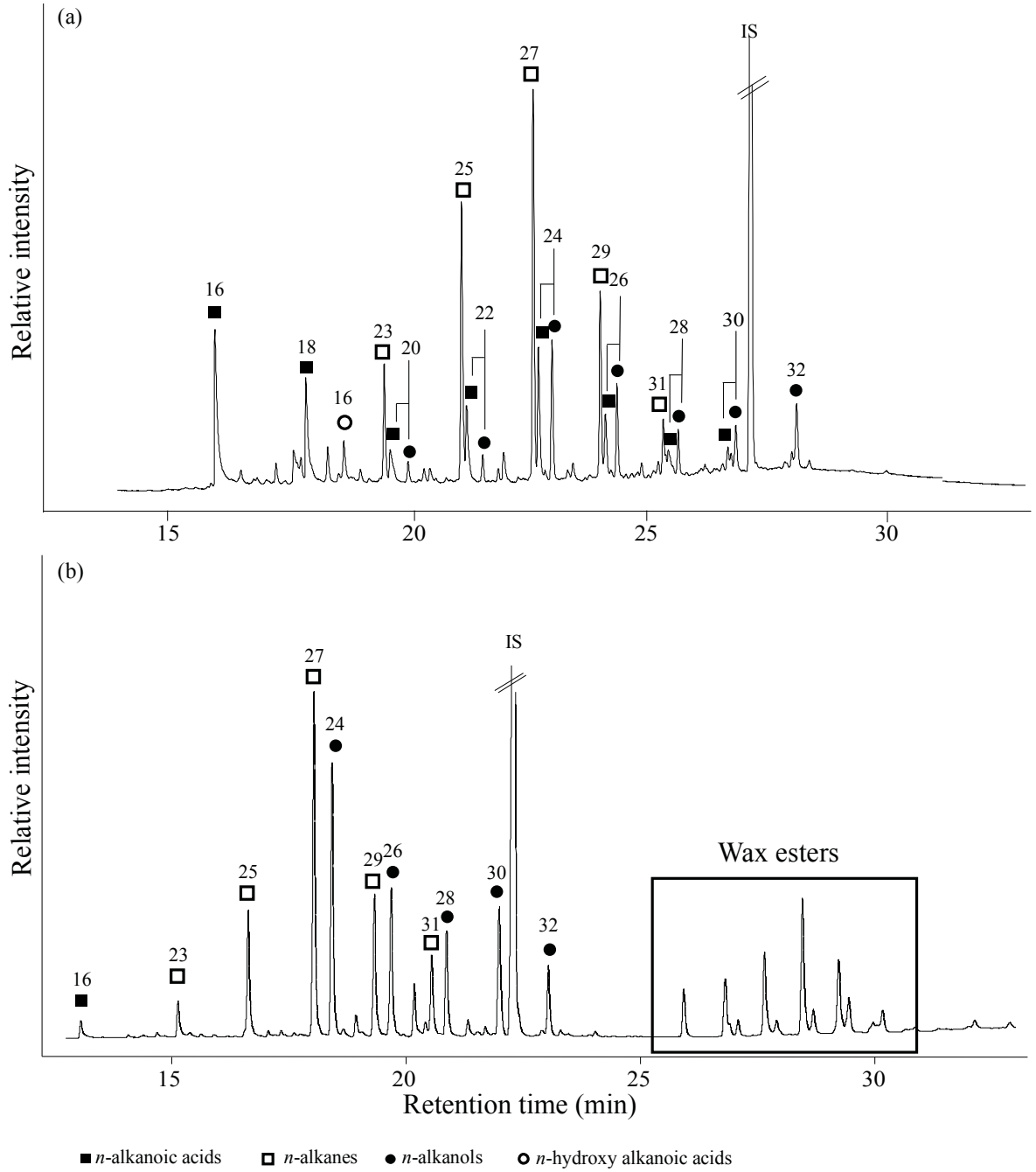

Figure 5-7: Partial high-temperature gas chromatograms of the potsherd ROS-C-2144 extracted using methanol/sulfuric acid (a) and, with chloroform/methanol (b) and showing beeswax biomarkers. IS is the internal standard the numbers correspond to the carbon chain length of the biomarkers.

These were reanalysed using solvent extraction and analysis by HT-GCMS, with 14 % (n = 16) of those potsherds from Bischoffsheim and 7% (n = 5) of those potsherds from Rosheim being found to contain even-carbon numbered wax monoesters and hydroxymonoesters (C_{40} to C_{50}), characteristic of beeswax (Heron *et al.* 1994; Regert *et al.* 2001; Roffet-Salque *et al.* 2015). The remaining pottery vessels analysed by HT-GCMS (n = 26; both sites) did not contain detectable wax esters characteristic of beeswax.

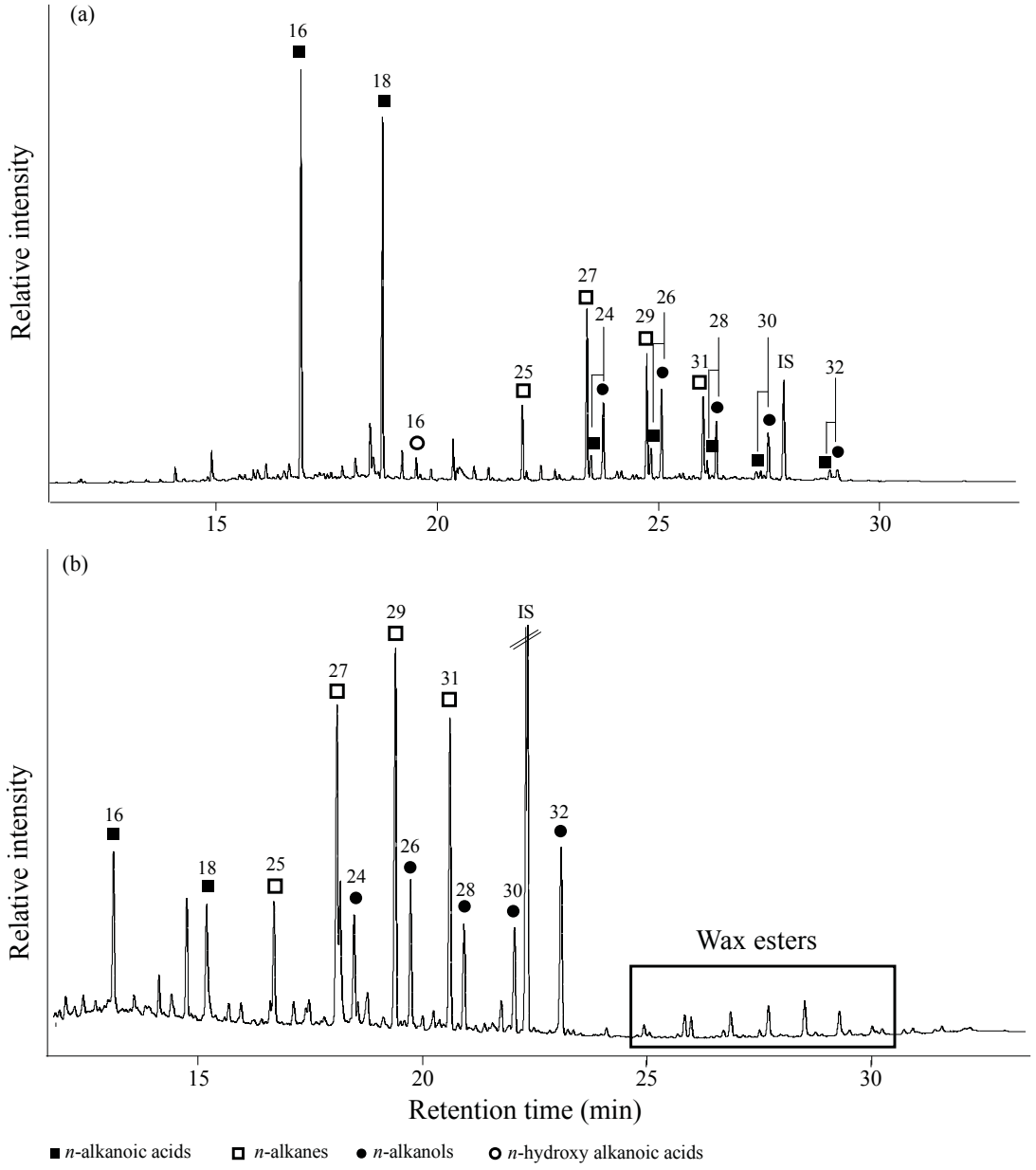

Figure 5-8: Partial high-temperature gas chromatograms of the TLEs of potsherd BIS-C-5297 showing beeswax biomarkers probably mixed with animal products extracted with, (a) methanol/sulfuric acid, and (b) chloroform/methanol. IS is the internal standard and numbers correspond to the carbon chain length of the biomarkers.

A number of the TLEs (ca. 20), extracted by the acid extraction method, show the additional presence of the $C_{18:0}$ FA in concentrations similar to the $C_{16:0}$ FA (Figure 5-8; e.g. BIS-C-5297), suggesting the mixing of animal products and beeswax in the same pottery vessel (Charters *et al.* 1995). Beeswax mixed with animal products (denoted by the presence of high abundances of the $C_{18:0}$ FA) were confirmed by detection of wax esters with HTGC-MS analysis in 3 % (n = 8) of potsherds from Bischoffsheim and 4 % (n = 3) from Rosheim. This lipid distribution, characteristic of beeswax, was recovered from both decorated and undecorated vessels.

Three decorated pottery vessels (BIS-C-5283, BIS-C-5284 and BIS-C-5286) from Bischoffsheim showed an unusual lipid distribution, dominated by odd-over-even carbon numbered *n*-alkanes (C_{25} to C_{31}) and long-chain *n*-alkanoic acids (C_{20}-C_{30}; Figure 5-9). Sherd BIS-C-5283 also showed the additional presence of *n*-alkanols (C_{18}-C_{32}). These lipid distributions all suggest the processing of plants (Eglinton and Hamilton 1967; Diefendorf *et al.* 2011).

The *n*-alkanes with chain lengths maximising at C_{29} suggest the processing of C_3 plants, rather than C_4 or aquatic plants in these vessels (Rommerskirchen *et al.* 2006). Evidence of plant lipid residues denoting plant processing is rarely found in pottery vessels but was recently reported from the African Neolithic (Dunne *et al.* 2016). Interestingly, these sherds all come from the same lateral pit (Pit 1201), suggesting differential food processing at the House 28 related to this pit, in contrast to the rest of the site.

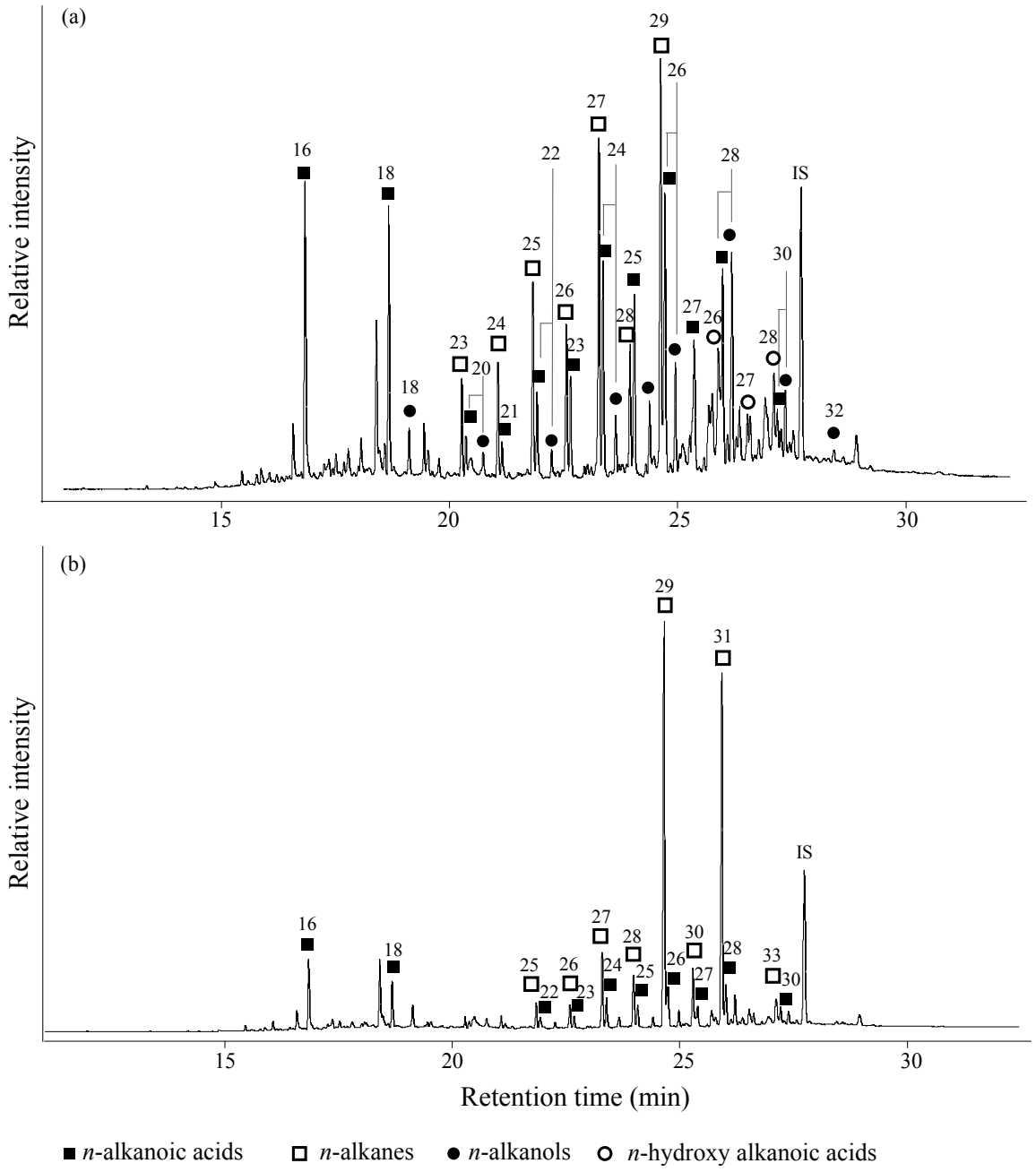

Figure 5-9: Partial high-temperature gas chromatograms of the potsherd (a) BIS-C-5283 and (b) BIS-C-5284 showing plant biomarkers. IS is the internal standard, numbers correspond to the carbon chain length of the biomarkers.

Despite the presence of C_{18} DHYA in ca. 100 potsherds, no evidence for long-chain DHYAs (C_{20} and C_{22}), or APAAs characteristic of aquatic resources (Hansel *et al.* 2004; Hansel and Evershed 2009), were detected in the potsherds. This suggests that aquatic products, from adjacent rivers, were not exploited. Based on biomarker analyses, potsherds from these two sites containing lipids characteristic of animal fats are good candidate for ^{14}C dating.

5.4.1.3 Stable carbon isotope analyses

The $\delta^{13}C$ values of the palmitic and stearic acids were determined by GC-C-IRMS (Section 2.4.3) in order to identify the sources of the animal products (Section 1.1.2.3.2) extracted from 103 potsherds (n = 36 for Rosheim and n = 67 for Bischoffsheim; Figure 5-10).

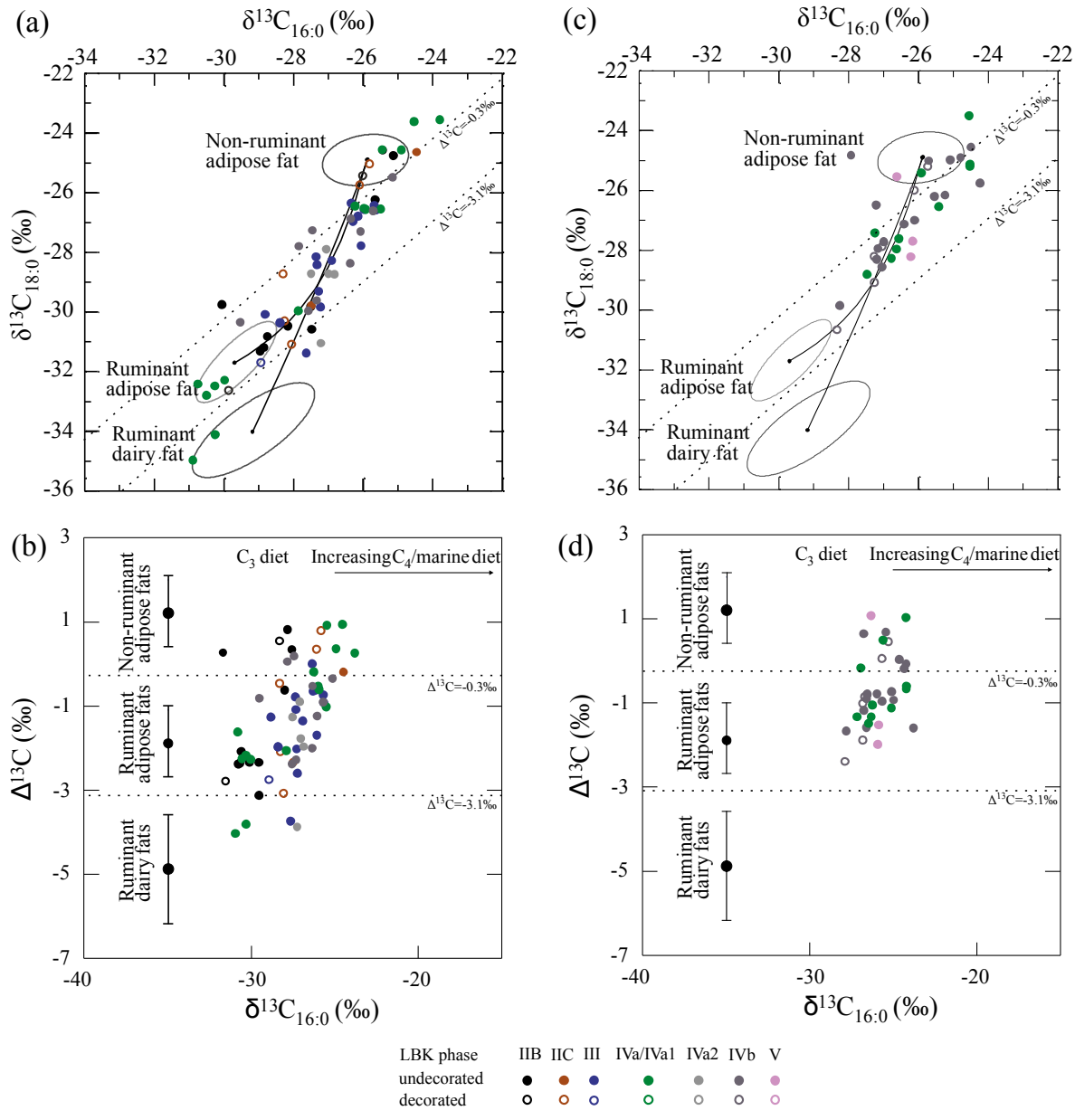

Figure 5-10: (a), (c) Scatter plots showing the $\delta^{13}C$ values for $C_{16:0}$ and $C_{18:0}$ fatty acids from animal products and (b), (d) $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$– $\delta^{13}C_{16:0}$) plotted against the $\delta^{13}C_{16:0}$ values present within the same potsherds from Bischoffsheim and Rosheim, respectively. Ellipses and ranges denote the values for modern reference fats from animal raised on C_3 diets (Copley *et al.* 2003).

5.4.1.3.1 Bischoffsheim

Significantly, at the site of Bischoffsheim, the $C_{16:0}$ and $C_{18:0}$ fatty acids display $\delta^{13}C$ values characteristic of non-ruminant adipose (n = 7), ruminant adipose (n = 9) and ruminant dairy fats (n = 2; Copley *et al.* 2003; Figure 5-10a, b), as well as mixtures of those products (n = 44) and the remaining (n = 4) plot outside the mixing lines but in proximity to the reference ellipses. The plotting of 19 lipid extracts in the reference ellipses suggests that ruminant animals were grazed on C_3 plants and that the values shifted from the ellipses are more likely due to some mixing of ruminant and non-ruminant adipose products rather than an environmental effect due to aridity (removed by the $\Delta^{13}C$ proxy; Mukherjee *et al.* 2005; Dunne *et al.* 2012). No plant remains evidence suggest an arid environment at the site or the region. Therefore, as a conservative approach, here and in the rest of the chapter, all $\delta^{13}C$ data points shifted from the reference ellipses will be considered as a mixture between ruminant and non-ruminant products rather than due to an environmental effect. Interestingly, the data points plotting in the ellipses also indicate some vessel specialisation for these particular animal products.

During phase IIB, four potsherds (BIS-C-5202, BIS-C-5203, BIS-C-5204 and BIS-C-5321) plot in the ruminant adipose ellipse, two (BIS-C-3998, BIS-C-4004) in the non-ruminant adipose ellipse, four (BIS-C-5201, BIS-C-4002, BIS-C-3394, BIS-C-5210) plot along the mixing lines between ruminant and non-ruminant ellipses and the remaining sample (BIS-C-5237) plotted outside the reference ellipses but not along the mixing lines, thus the source of such fat is unclear.

During phase IIC three potsherds (BIS-C-5212, BIS-C-5324, BIS-C-5325) present $\delta^{13}C$ values characteristic of non-ruminant adipose fats and the remaining four plots along the mixing lines close to the ruminant adipose ellipse suggesting a dominance of such products in the TLEs.

During phase III, all of the lipid residue $\delta^{13}C$ values plot along the mixing lines although three potsherds (BIS-C-5301, BIS-C-4515, BIS-C-5299) plot at the edge of the ruminant adipose products ellipse, suggesting the vessel was mainly used to process this product. In addition, potsherd BIS-C-4514, showed a $\Delta^{13}C$ value of -3.8 ‰ suggesting a dominance of dairy mixed with non-ruminant carcass product. These data suggest that there is no vessel specialisation during phase III.

During phase IVa1, the majority of the lipid residues plot in the reference ellipses, with two plotting as non-ruminant adipose products (BIS-C-4531, BIS-C-4519), four (BIS-C-4518, BIS-C-4520, BIS-C-4521, BIS-C-4522) in the ruminant adipose ellipse and two (BIS-C-4527, BIS-C-4528) in the dairy product ellipse. The other five potsherds plot along the mixing lines with likely a dominance of ruminant adipose products for BIS-C-4524 and a dominance of non-ruminant adipose fats for the remaining three. Two potsherds (BIS-C-4519, BIS-C-4537) exhibit $\delta^{13}C$ values more enriched than the non-ruminant ellipse, which could suggest the use of marine products, but it is unlikely considering the distance of the site from for the coast, thus it could correspond to statistical outliers of non-ruminant products.

During phase IVa2, all lipid residue $\delta^{13}C$ values lie along the mixing lines between ruminant and non-ruminant adipose product. The vessel BIS-C-4544 exhibits a $\Delta^{13}C$ value of -3.9 ‰ suggesting a dominance of dairy mixed with non-ruminant carcass products, but with a dominance of dairy product processing. These data show that there was no vessel specialisation.

During phase IVb, all the potsherds plot along the mixing lines between the ruminant and non-ruminant products ellipses with potsherd BIS-C-4556 being located at the edge of the ruminant

adipose ellipse and BIS-C-4063 at the edge of the non-ruminant adipose ellipses, suggesting the dominance of such products. These data show that there is no vessel specialisation

In summary, vessel specialisation for certain animal products was visible, in particular, for the phases IIB and IVa1 at Bischoffsheim. This could be related to the houses related to the contexts analysed (House 32 and 26). Two TLEs plot in the dairy product ellipse (BIS-C-4527 and BIS-C-4528), both from phase IVa1, possibly suggesting the start of dairying at this phase. Two additional sherds from phase III and IVa2 (BIS-C-4514: -3.8 ‰, BISC-C-4544: -3.9 ‰) suggested some mixing of dairying and non-ruminant adipose products. It is possible that dairying products were also present in the following phases, however, a dairy signal could be 'masked' if it is mixed with non-ruminant adipose products. Finally, no $\delta^{13}C$ values of the $C_{16:0}$ and $C_{18:0}$ provided evidence for processing freshwater aquatic product at the site.

5.4.1.3.2 Rosheim

At the site of Rosheim, the $C_{16:0}$ and $C_{18:0}$ fatty acids display $\delta^{13}C$ values characteristic of non-ruminant adipose processing (n = 6), as well as some mixing of non-ruminant and ruminant products (n = 27; Copley *et al.* 2003; Figure 5-10c, d).

During phase IVa one vessel plots in the non-ruminant product ellipse (ROS-C-2155), with another just outside the ellipse (ROS-C-2168) suggesting a dominance of this product. Potsherd ROS-C-2158 exhibits more enriched values, usually characteristic of marine products but this is unlikely due to the inland location of the site. The remaining samples (n = 6) plot along the mixing lines between non-ruminant and ruminant adipose products.

During phase IVb four potsherds plot in the ellipses of non-ruminant adipose products (ROS-C-2183, ROS-C-4668, ROS-C-4694, ROS-C-4700) and three just outside the ellipses

(ROS-C-2187, ROS-C-2194, ROS-C-4690), suggesting the dominance of such products. The remaining potsherds plot along the mixing lines of non-ruminant and ruminant adipose fats with two (ROS-C-4688, ROS-C-4698) plotting close to the ruminant adipose product ellipse, suggesting the dominance of such source.

The three potsherds from phase V plot in the non-ruminant adipose ellipse (ROS-C-2145) or along the mixing lines with ruminant adipose products (ROS-C-2143, ROS-C-2154).

Unlike the site of Bischoffsheim no evidence for dairy products or their mixing with non-ruminant adipose products were visible. However, similar to the site of Bischoffsheim no evidence for freshwater aquatic product processing can been seen at Rosheim. Based on $\delta^{13}C$ analyses the potsherds with animal fats from both sites are good candidates for CSRA despite mixing between ruminant and non-ruminant products in a majority of the potsherds.

5.4.1.4 Comparison with archaeozoological data

The faunal assemblages, comprising 1,000 and 3,000 animal bones from Bischoffsheim (unpublished data from R-M. Arbogast) and Rosheim, respectively (Arbogast 2000; Lefranc and Michler 2015), are dominated by domesticated animal remains, mainly cattle, caprines and pigs (Appendix 6-7). Domesticated animal bones comprise 93.2 % of the number of identified specimen (NISP) at Rosheim. At Bischoffsheim, the domesticated bones comprise 86.7 % NISP for the Early phase, 92.9 % NISP for the Middle phase and 92.4 % NISP for the Late phase.

The $\delta^{13}C$ values of the $C_{16:0}$ and $C_{18:0}$ FAs show the presence of ruminant adipose and non-ruminant adipose products. Here, the $\delta^{13}C$ values are compared to the liveweight values derived from the faunal assemblages at both sites (as follows). The availability of ‘meat’ per animal

species (e.g. cattle) is directly related to its liveweight. This 'meat' availability can be approximated based on standards liveweight, i.e. 37.5 kg for a sheep (1 unit), 275 kg for a cow (7.33 unit) and 87.5 kg for a pig (2.33 unit) which were determined on an archaeological site from 3rd century BC in Germany (Boessneck *et al.* 1971) then applied to 8th Millennium AD in UK (O'Connor 1991), and more recently to Neolithic Greece (Whelton 2016). Based on this observation, more carcass products would be available from a cow and a pig than a sheep, therefore, by weighting the number of faunal remains recovered at sites for the liveweight (or mass) of the animal, an estimation of the availability of 'meat' or carcass product per species at a site can be obtained and compared to the lipid residues present in pottery vessels (O'Connor 1991 from Boessneck *et al.* 1971; Figure 5-11). The estimation of 'meat' yield would not necessarily be accurate for animals from the LBK compared to Roman times, however, this approximation would better approach the reality than using NISP on animal remains.

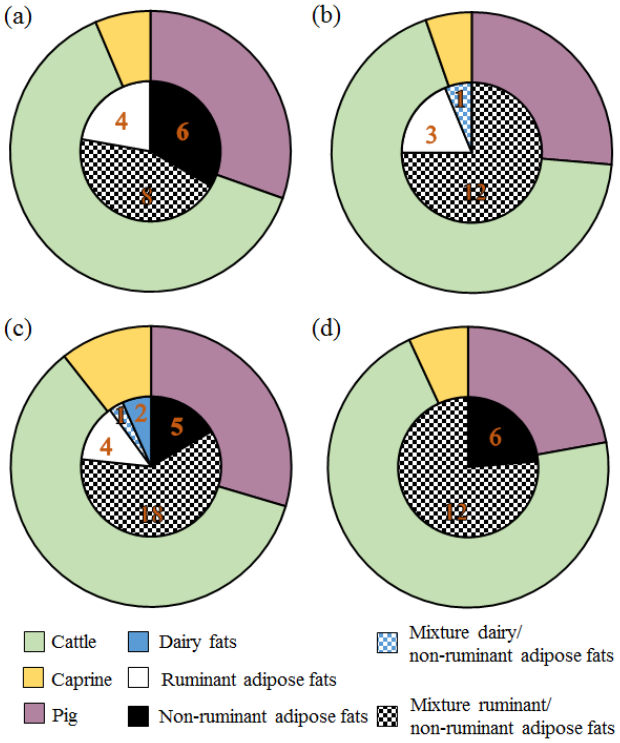

Figure 5-11: The outer circle is the meat weight percentage of domesticated animals and the inner circle is the percentage of animal products recovered in potsherds based on $\delta^{13}C$ values of FAs at Bischoffsheim for the (a) Early LBK (IIB, IIC), (b) Middle LKB (III), (c) Late LBK (IVa1, IVa2, IVb) and at Rosheim (d) for the Late and Final LBK (IVa, IVb, V). The animal remains are weighted based on the availability of meat per animal, cattle = 7.33, pig = 2.33, sheep/goat = 1 (O'Connor 1991).

The conversion of the number of species remains for the meat weight available at the sites, obtained from the faunal assemblage, demonstrates that there are, overall, more carcass products available from ruminant animals (ca. 60-70 % of cattle and ca. 5-10% of caprines) than from pigs (ca. 30 %).

5.4.1.4.1 Bischoffsheim

For the Early LBK phase at Bischoffsheim (Figure 5-11.a), there is a good correlation between the weighted number of pig remains (30 %, NISP (number of identified specimen) and the proportion of non-ruminant products in pottery vessels (33 %). The cattle comprise 63 % of the meat weight and sheep 6 %, however, a total of 22 % of the $\delta^{13}C$ pottery FAs values are indicative of ruminant adipose product processing, suggesting an underestimation of the ruminant carcass product processing. This is likely due to the mixing of both ruminant and non-ruminant carcass products (44 %) in the same vessels.

For the Middle LBK at Bischoffsheim (Figure 5-11b), cattle comprise 68 % of the meat weight and sheep 6 %, however, only 15 % of the $\delta^{13}C$ FAs values are indicative of predominantly ruminant adipose product processing, suggesting an underestimation of the ruminant carcass product processing. The faunal remains of pig translate to 26 % of the meat weight but no FAs $\delta^{13}C$ values plotted in the porcine reference ellipses. The contribution of ruminant and non-ruminant carcass products processing is likely underestimated by lipid residue analysis due to the mixing of both non-ruminant and ruminant carcass (75 %) or dairy (5 %) products in the same vessels.

For the Late phase of the LBK at Bischoffsheim (Figure 5-11c), more pig carcass products would have been available (30%) than non-ruminant products (17 %) as shown by the FAs $\delta^{13}C$ values. The cattle comprise 60 % of the meat weight and the sheep 11 %, however, a total

of 13 % of the FAs $\delta^{13}C$ values are indicative of ruminant adipose product processing, suggesting an underestimation of the ruminant carcass product processing. These underestimations of carcass products are likely due to the mixing of both ruminant and non-ruminant carcass products (65 %) in the same vessels.

5.4.1.4.2 Rosheim

At Rosheim (Late LBK; Figure 5-11,d), there is a good correlation between the weighted number of pig remains (22 %) and the proportion of non-ruminant products in pottery vessels (24 %). The $\delta^{13}C$ values of FAs (76 %) show some mixing between non-ruminant and ruminant adipose products suggesting that the amount of ruminant carcass products (cattle: 71 % and sheep: 7 % of the meat weight) processed in pottery vessel is underestimated.

These faunal data confirm that the enriched $\delta^{13}C$ values obtained from the FAs are due to the contribution of porcine products in potsherds. The absence of dairy products and the dominance of mixing of ruminant and non-ruminant carcass products suggests that the majority of domesticated animals were raised for their primary products. Thus, based on $\delta^{13}C$ values compared with faunal remains, the potsherds containing animal fats are good candidates for CSRA as they are unlikely to come from an aquatic resource.

5.4.2 Lipid residue analysis of Middle Neolithic sites from the Lower Alsace

5.4.2.1 Site description

The site of Rosheim, “Mittleweg”, “Sandgrube” and “Laser”, situated in the Lower Alsace north to the Rosenmeer stream, comprises Middle Neolithic settlements from the Grossgartach and Roessen culture (Jeunesse and Arbogast 1996; Lefranc *et al.* 1999; Appendix 6-8 and 6-9). Several pits from the cultures of Grossgartach (~ 30) and Roessen (~ 10), were excavated, but

no house plan was discovered. The site (at the time of the excavation) yielded the largest pottery assemblages ever found in the region for the two Middle Neolithic culture. More recently, in the same geographical area, a Grossgartach necropolis (locality "Rosenmeer") was excavated and a program of dating was carried out (Jeunesse *et al.* 1996).

5.4.2.2 GC and GC-MS analyses

A total of 57 potsherds from the Grossgartach and 29 potsherds from the Roessen cultures were selected (Sections 2.3.2, 2.4.1, 2.4.2; Appendix 6-10). Total lipid extracts with concentrations >5 $\mu g.g^{-1}$ were recovered from 98 % (n = 56) of potsherds, with an average concentration of 659 $\mu g.g^{-1}$ for the Grossgartach and 93 % (n = 27) of the potsherds with an average concentration of 418 $\mu g.g^{-1}$ for the Roessen. Many potsherds from both cultures showed high lipid concentrations >1 $mg.g^{-1}$ of sherd (e.g. ROS-C-4629: 2.0 $mg.g^{-1}$; ROS-C-4600: 4.4 $mg.g^{-1}$; ROS-C-4644: 6.1 $mg.g^{-1}$) demonstrating good preservation of lipids.

A number of the TLEs were dominated by the presence of $C_{16:0}$ and $C_{18:0}$ FAs characteristic of degraded animal fats (Figure 5-12a). This corresponds to 45 % (n = 25) of the TLEs for the Grossgartach and 37 % (n = 10) for the Roessen group. The odd-numbered $C_{17:0}$ FA and *iso*- and *anteiso*-isomers, possibly indicative of microbial activity in the rumen, and characteristic of a ruminant product origin, was also present (n = 21; Keeney *et al.* 1962).

Lipid profile of a number of TLEs, exhibited even-carbon numbered *n*-alcohols (C_{24} to C_{32}), odd-carbon numbered *n*-alkanes (C_{23} to C_{33} maximizing at C_{27}), even-numbered FAs ($C_{16:0}$ then C_{24} to C_{36}), characteristic of beeswax after hydrolysis (Regert *et al.* 2001; Correa-Ascencio and Evershed 2014; Figure 5-12b; e.g. ROS-C-4601, ROS-C-4615). These sherds were re-analysed after conventional solvent extraction by HT-GCMS, with 9 % (n = 5) and 15 % (n = 4) of the potsherds from the Grossgartach and the Roessen, respectively, being found to contain

even-carbon numbered wax monoesters and hydroxymonoesters (C_{40} to C_{50}), characteristic of beeswax (Heron *et al.* 1994; Regert *et al.* 2001; Roffet-Salque *et al.* 2015). Beeswax biomarkers were detected in both decorated and undecorated vessels. Beeswax mixed with animal products (marked by the additional presence of high $C_{18:0}$ FA) were identified in 2 potsherds (ROS-C-4606 and ROS-C-4617).

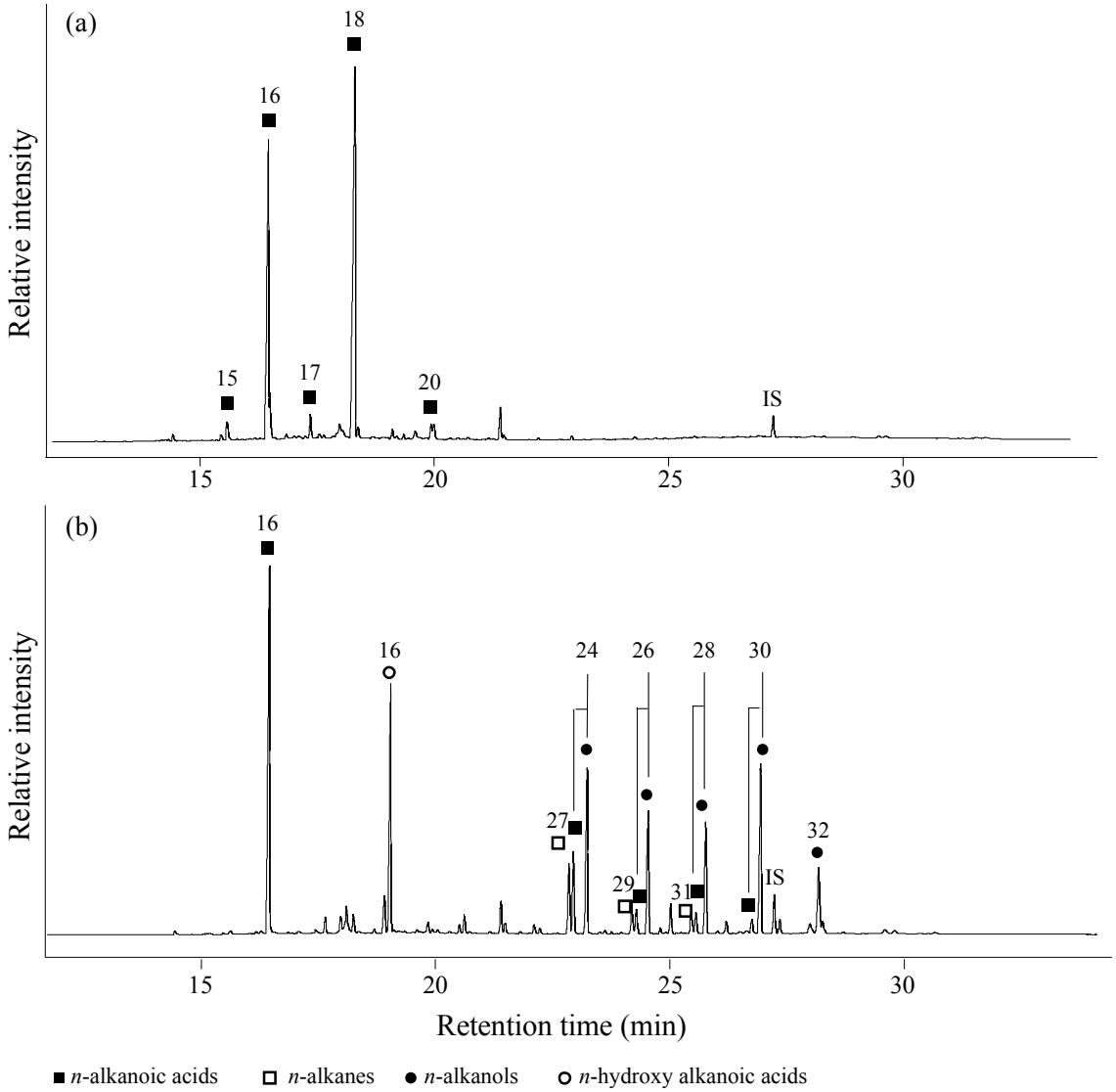

Figure 5-12: Partial gas chromatogram of the potsherd (a) ROS-C-4002 showing a lipid distribution characteristic of degraded animal products, and (b) ROS-C-4615 showing lipids ascribable to beeswax. IS is the internal standard and the numbers correspond to the carbon chain length of the biomarkers.

No evidence for long chain DHYAs, characteristic of aquatic resource exploitation were detected, suggesting that freshwater products from local river streams were not exploited

(Hansel and Evershed 2009). Based on biomarker analyses, potsherds containing animal fats are good candidate for ^{14}C dating.

5.4.2.3 Stable carbon isotope analyses

The $\delta^{13}C$ values of the palmitic and stearic acids were determined by GC-C-IRMS (Section 2.4.3) in order to identify the sources of the animal products extracted from 25 potsherds for the Grossgartach and 10 for the Roessen (Figure 5-13; Section 1.1.2.3.1).

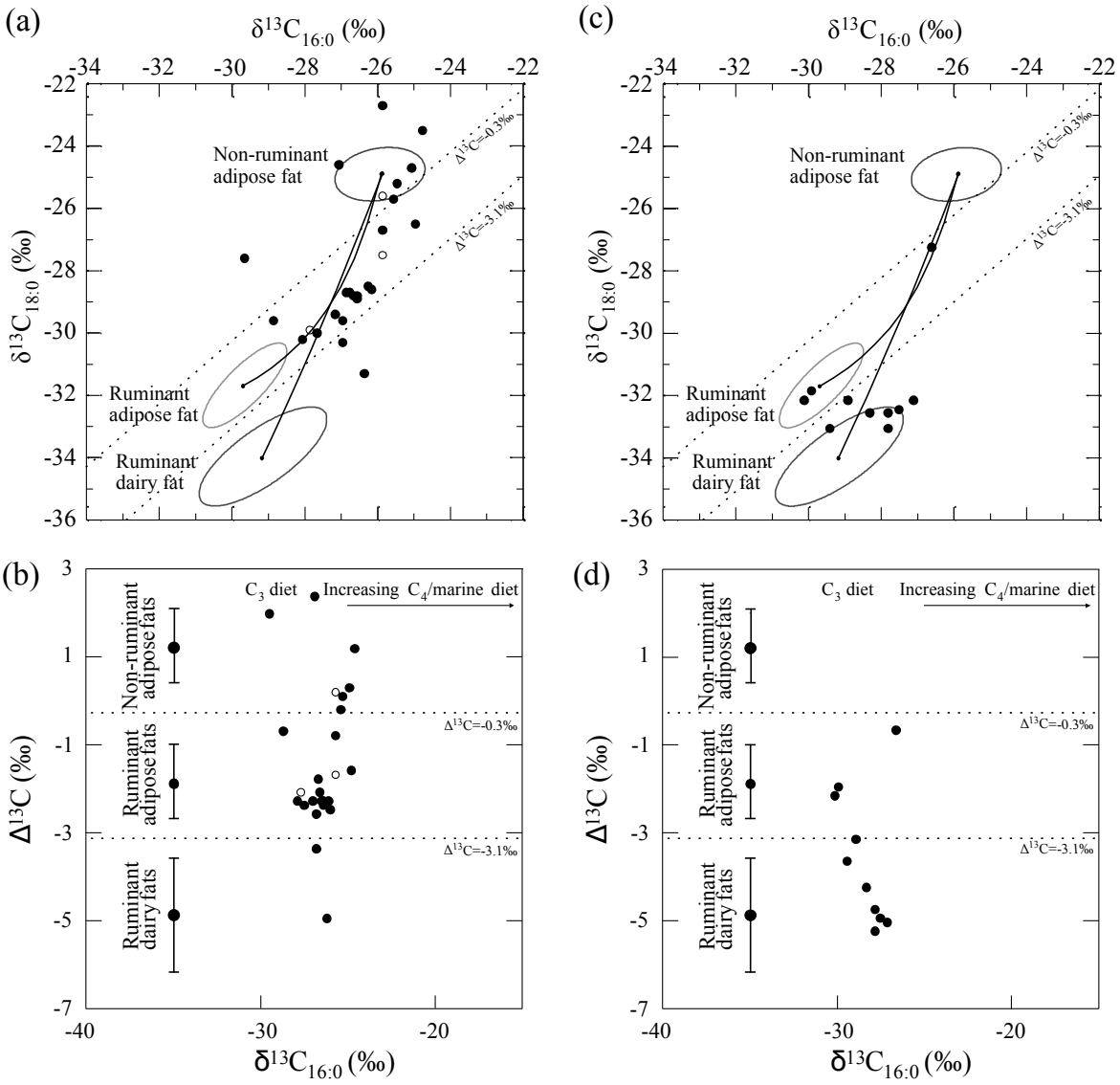

Figure 5-13: (a), (c) Scatter plots showing the $\delta^{13}C$ values for $C_{16:0}$ and $C_{18:0}$ fatty acids from animal products and (b), (d) $\Delta^{13}C$ values ($\delta^{13}C_{18:0}$– $\delta^{13}C_{16:0}$) plotted against their $\delta^{13}C_{16:0}$ values present within the same potsherds from the Grossgartach and the Roessen, respectively. Ellipses and ranges denote the values for modern reference fats from animals raised at C_3 diet (Copley *et al.* 2003).

5.4.2.3.1 Grossgartach

Significantly, for the Grossgartach culture, the majority of $C_{16:0}$ and $C_{18:0}$ fatty acids display $\delta^{13}C$ values characteristic of non-ruminant adipose product processing (n = 5), with others showing evidence of some mixing between non-ruminant and ruminant products (n =16; Figure 5-13a,b). No TLEs plot in the ruminant product ellipses. Two sherds (ROS-C-4641, ROS-C-4664) present $\delta^{13}C$ values more enriched than the non-ruminant values which could suggest a contribution from marine resources, but it is unlikely considering the inland location of the site. One sherd (ROS-C-4654: $\Delta^{13}C$ = 2 ‰) is outside the reference ellipses but not along the mixing lines, thus its source is unclear and perhaps suggest some freshwater products exploitation (Cramp and Evershed 2014). Two sherds (ROS-C-4616: -3.4 ‰, ROS-C-4650: -5.0 ‰) showed a $\Delta^{13}C$ value below -3.1 ‰, which could suggest a dominance of dairying products mixed with non-ruminant adipose products, but with a dominance of dairy products.

5.4.2.3.2 Roessen

During the Roessen culture the $C_{16:0}$ and $C_{18:0}$ fatty acids display $\delta^{13}C$ values characteristic of ruminant dairy (n = 5), with one potsherd at the edge of the dairy ellipse (ROS-C-4617) and ruminant adipose fats (n = 2; Copley *et al.* 2003; Figure 5-13c, d), supporting an interpretation of vessel specialisation and no environmental effect in the region (Section 5.4.1.3). One lipid residue (ROS-C-4629) plots in between the ruminant adipose and dairy ellipse and one potsherd (ROS-C-4628) suggests the mixing of ruminant with non-ruminant products. No further evidence for non-ruminant products being processed in potsherds was recovered.

These data suggest a significant difference in subsistence and animal management systems between the Grossgartach to the Roessen cultural groups, with the former specialising in carcass products and the other in dairy products. Neither of the cultures presented $\delta^{13}C$ values

suggesting the use of freshwater resources from adjacent river streams, at the exception of ROS-C-4654 (Cramp and Evershed 2014), and are good candidates for CSRA despite mixing between ruminant and non-ruminant products during the Grossgartach.

5.4.2.4 Comparison with archaeozoological data

The faunal assemblage for the culture of Grossgartach (~2,000 remains identified) and Roessen (~500 identified) are dominated by domesticated animals remains which comprises 93.2 % NISP of the faunal assemblage for the Grossgartach and 93.2 % NISP for the Roessen (Appendix 6-7; Jeunesse and Arbogast 1997; Lefranc *et al.* 1999). The relative proportion of different animals remains are similar for the Grossgartach and the Roessen, however, significantly fewer animal remains were found with the Roessen (Jeunesse and Arbogast 1997; Lefranc *et al.* 1999).

The liveweight values derived from the faunal assemblages were compared to the $\delta^{13}C$ values of FAs (O'Connor 1991; Figure 5-14, see Section 5.4.1.4).

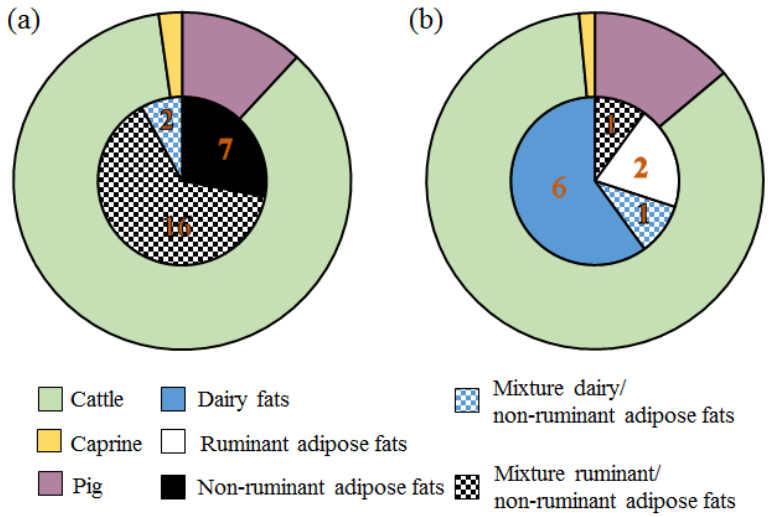

Figure 5-14: The outer circle is the meat weight percentage of domesticated animals and the inner circle is the percentage of animal products recovered in potsherds based on $\delta^{13}C$ values of FAs at Rosheim for (a) Grossgartach group and (b) Roessen group. The animal remains have been weighted with the availability of meat per animal, cattle = 7.33, pig = 2.33, sheep/goat = 1 according to O'Connor 1991).

The conversion of the number of species remains for the meat weight available at the sites, obtained from the faunal assemblage, demonstrates that there are, more carcass products available from cattle (ca. 70 %) than caprines (ca. 1 %) and pigs (ca. 12 %). It should be noted that the proportion of pig carcass product weight for both Middle Neolithic groups is less than half that of the LBK faunal assemblage (ca. 30%).

5.4.2.4.1 Grossgartach

During the Grossgartach culture (Figure 5-14a), more non-ruminant carcass products (28 %) are recovered in potsherds than pig carcass products (12 %). It is, however, difficult to evaluate if such difference is significant as carcass products availability corresponds to an estimation which is not necessarily precise or if it suggests the use of marine products (but as mentioned previously this is unlikely). The remainder of the FAs $\delta^{13}C$ values comprises mixing of non-ruminant with ruminant adipose (64 %) or with dairy (8 %) products. It is, therefore, difficult to correlate between the ruminant remains (cattle: 86 %, caprines: 2 % of the meat weight) and $\delta^{13}C$ values characteristics of ruminant adipose products in pottery vessels. Thus, based on $\delta^{13}C$ values and faunal remains, these potsherds are potential candidates for CSRA.

5.4.2.4.2 Roessen

There are no $\delta^{13}C$ values characteristic of non-ruminant carcass products in the Roessen potsherds, except for one potsherd showing a mixture of ruminant and non-ruminant products, suggesting a very limited use of this food source (4 %; Figure 5-14b). However, the pig remains represent 14 % of the carcass products by weight. This could suggest that pig products were not processed in pots, but possibly cooked by some other method, such as roasting (e.g. such underestimation of porcine residues in potsherds despite high number of pig remains suggesting different culinary practices was previously highlighted in British Neolithic Grooved

Ware site; Mukherjee *et al.* 2008). Approximately 22 % of the $\delta^{13}C$ values of the lipid residues correspond to ruminant carcass products which are likely to be of cattle origin, due to the minimal availability of caprine carcass products. However, as the economy relies mainly on dairy products (67 % of the lipid residues), there is no straightforward relation between the quantity of carcass products available and processed in pottery vessels (revealed by ORA). An economy based on dairy suggests that more (female) animals were kept alive for their secondary products (Vigne and Helmer 2007). Such herd management strategies for dairy exploitation could also be supported by the lower number of animal remains present in the Roessen (ca. 500), as opposed to the Grossgartach assemblage (ca. 2000). Thus, based on $\delta^{13}C$ values compared with faunal remains, the potsherds containing animal fats are potential candidates for CSRA.

5.4.3 Lipid residue analysis of Early Neolithic sites from the Upper Alsace

5.4.3.1 Sites description

Three sites from UA were sampled. The first excavation at the border site of Colmar "Route de Rouffach" revealed a number of pits containing pottery material from Early, Middle and Late LBK phases (Bonnet *et al.* 1988) and the second excavation revealed 4 house structures (one well-preserved and 3 highly eroded) and one enclosure ditch dated to the Middle and Late LBK (Jeunesse 1993b; Appendix 6-11). Two distinct pottery assemblages by their decorative motifs were discovered. One assemblage corresponds to the Upper Alsace LBK pottery tradition and the other to the Lower Alsace pottery tradition, suggesting this might be a site of contact between the two regional groups.

The site of Ensisheim "Ratfeld", located ca. 10 km from the city of Mulhouse, was excavated in 1987, revealing only single pits and one grave from the LBK culture (Jeunesse and Sainty

1992; Appendix 6-12). Pottery vessel assemblages were recovered from 35 pits and were relatively dated by seriation to the Early to the Final phase of LBK of UA. Among these pits, the chronology was not necessarily homogeneous as a number of pits could be considered as transitional between two phases, furthermore, the Late and Final phases are not as well represented as the previous ones.

The site of Sierentz "Sandgrube and Tiergarten", located ca. 20 km from the city of Mulhouse, and excavated from 1981 to 2000, showed an occupation from the Early Neolithic to the Gallo-Roman period (Wolf 1999). A total of 15 houses from the Late and Final LBK phase were recognised (Lefranc 2001; Appendix 6-13) but two of them not excavated (5 and 15) and two houses with associated materials were not studied (8 and 9; Wolf *et al.* 1993; Siegler 1994; Schaltenbrand 1999; Lefranc 1999, 2001; Lefranc and Denaire 2000; Jeunesse *et al.* 2007).

5.4.3.2 GC and GC-MS analyses

A total of 192, 101 and 102 potsherds from Colmar, Ensisheim and Sierentz sites, respectively, were analysed (Sections 2.3.2, 2.4.1, 2.4.2; Appendix 6-14, 6-15 and 6-16). Total lipid extract concentrations >5 $\mu g.g^{-1}$ were obtained from 60 % (n = 115) of the potsherds from Colmar, 73 % (n = 73) from Ensisheim and 80 % (n = 82) from Sierentz. However, the site of Colmar, showed poor lipid preservation with approximatively 30% of the potsherds contaminated by the storage (i.e. plasticizers and modern distribution of even and odd-numbered alkanes from 11 atoms of C) and with a low average lipid concentration of 49 $\mu g.g^{-1}$. The TLEs from Ensisheim exhibited an average lipid concentration of 143 $\mu g.g^{-1}$ including three sherds with lipid concentrations above 1 $mg.g^{-1}$ of sherd (ENS-C-5913: 1.2 $mg.g^{-1}$; ENS-C-5934: 1.6 $mg.g^{-1}$; ENS-C-5940: 2.1 $mg\text{-}g^{-1}$) and the TLEs from Sierentz present an average lipid

concentration of 240 µg.g^{-1} including three sherds with lipid concentrations above 1 mg.g^{-1} of sherd (SIE-C-5344: 1.3 mg.g^{-1}; SIE-C-5364: 1.2 mg.g^{-1}; SIE-C-5380: 2.5 mg-g^{-1}).

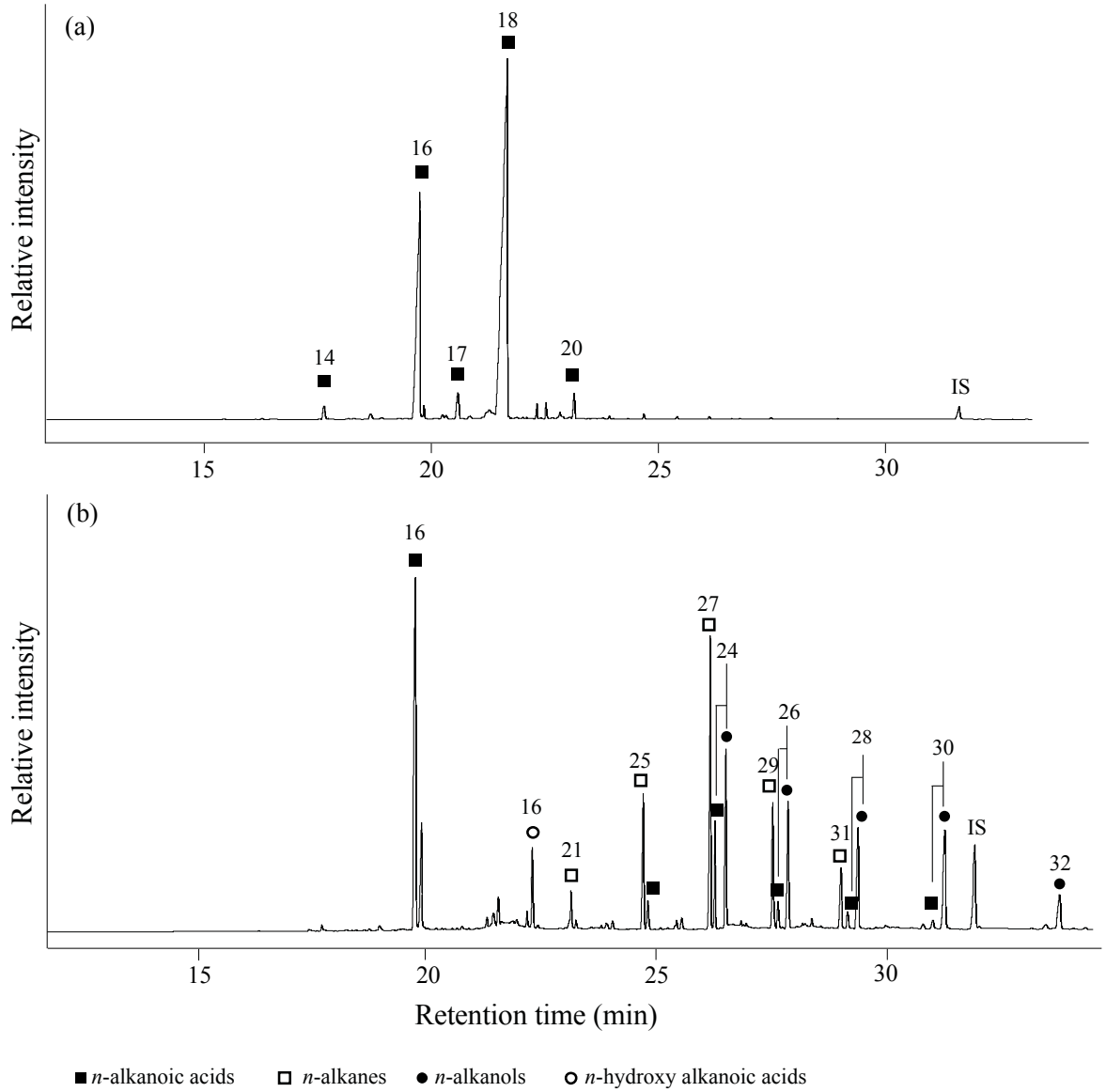

Figure 5-15: Partial gas chromatogram of the potsherd (a) ENS-C-5978 showing a lipid distribution characteristic of degraded animal products and (b) ENS-C-6008 showing lipids distribution attributable to beeswax biomarkers after hydrolysis. IS is the internal standard and the numbers correspond to the carbon chain length of the biomarkers.

A number of the TLEs were dominated by the presence of $C_{16:0}$ and $C_{18:0}$ FAs characteristic of degraded animal fats. This corresponded to 15 % (n = 17) of the TLEs for Colmar, 46 % (n = 46) for Ensisheim and 57 % (n = 45) for Sierentz (Figure 5-15a). The odd-numbered $C_{17:0}$ FA and *iso*- and *anteiso*-isomers, possibly indicative of microbial activity in the rumen and

characteristic of a ruminant product origin, was also present (ca. 60 potsherd; Keeney *et al.* 1962). In five potsherds (COL-C-6046, COL-C-6060, COL-C-6066, ENS-C-5980 and SIE-C-5344) the presence of odd-numbered ketones (31 to 35) formed by pyrolysis of FAs and ketonic decarboxylation suggests heating to high temperatures (Evershed *et al.* 1995; Raven *et al.* 1997).

A number of TLEs (10 % or $n = 11$, of the TLES from Colmar, 14 % or $n = 10$ from Ensisheim and 12 %, $n = 10$ from Sierentz) exhibited even-carbon numbered *n*-alcohols (C_{24} to C_{32}), odd-carbon numbered *n*-alkanes (C_{23} to C_{33} maximizing at C_{27}), even-carbon numbered FAs ($C_{16:0}$ then C_{24} to C_{36}), characteristic of beeswax after hydrolysis (Regert *et al.* 2001; Correa-Ascencio and Evershed 2014; Figure 5-15b). Beeswax mixed with animal products (suggested by the additional presence of high $C_{18:0}$ FA) were suggested but not detected in 25 potsherds as no high-temperature analysis were performed on those potsherds for the identification of wax esters. These lipid profiles were recovered in both decorated and undecorated vessels.

No evidence for long chain DHYAs, which are characteristic of aquatic resource exploitation was found, suggesting fresh water resources from local river streams were not exploited (Hansel and Evershed 2009). Based on biomarker analyses, the potsherds with animal fats residues are good candidate for ^{14}C dating.

5.4.3.3 Stable carbon isotope analyses

The $\delta^{13}C$ values of the palmitic and stearic acids were determined by GC-C-IRMS (Section 2.4.3) in order to identify the sources of the animal products extracted from 108 potsherds ($n = 17$ for Colmar, $n = 46$ for Ensisheim and $n = 45$ for Sierentz; Figure 5-16; Section 1.1.2.3).

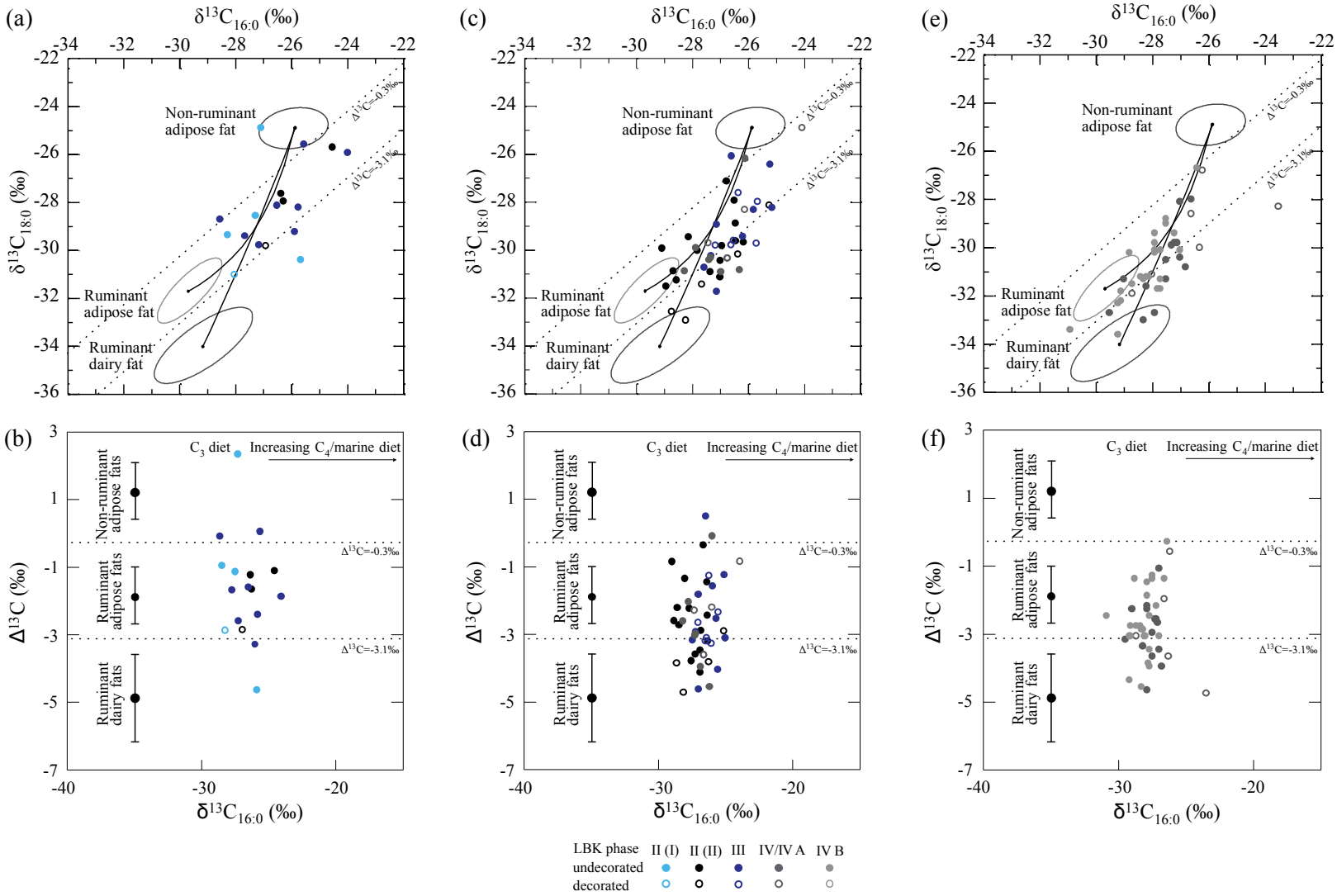

Figure 5-16: (a), (c), (e) Scatter plots showing the $\delta^{13}C$ values for $C_{16:0}$ and $C_{18:0}$ fatty acids from animal products and (b), (d), (f) $\Delta^{13}C$ values ($\delta^{13}C_{18:0} - \delta^{13}C_{16:0}$) plotted against their $\delta^{13}C_{16:0}$ values present within the same potsherds from Colmar, Ensisheim and Sierentz, respectively. Ellipses and ranges denote the values for modern reference fats from animal raised at C_3 diet (Copley *et al.* 2003).

5.4.3.3.1 Colmar

At the site of Colmar the $C_{16:0}$ and $C_{18:0}$ fatty acids displayed $\delta^{13}C$ values characteristic of non-ruminant products ($n = 2$) and their mixing with ruminant products ($n = 15$; Copley *et al.* 2003; Mukherjee *et al.* 2005; Figure 5-16a, b). The two potsherds with non-ruminant products came from phase I (COL-C-6025) and III (COL-C-6058). In addition, two sherds from phase I (COL-C-6118: -4.7 ‰) and phase II (COL-C-6060: -3.3 ‰) showed a $\Delta^{13}C$ value below -3.1 ‰ which would support some mixing non-ruminant adipose products with a dominance of dairying products. No significant difference between the phases were visible.

5.4.3.3.2 Ensisheim

At the site of Ensisheim, the FAs displayed $\delta^{13}C$ values plotting in the reference ellipses of ruminant adipose ($n = 3$) and ruminant dairy products ($n = 2$; Figure 5-16c, d) suggesting some vessel specialisation and once again no environmental effect. The remaining potsherds $\delta^{13}C$ values plot along the mixing lines with non-ruminant products ($n = 39$) and one potsherd plotted close to the reference ellipse of non-ruminant (ENS-C-5985) suggesting the dominance of such products.

The two extracts (ENS-C-5919, ENS-C-5933) plotting in the dairy ellipse and the three in the ruminant adipose ellipse (ENS-C-5921, ENS-C-5946, ENS-C-5940) were from the phase II at Ensisheim, suggesting some vessel specialisation of this phase. Seven potsherds present TLE profiles with a $\Delta^{13}C$ value below -3.1 ‰ suggesting the mixing of non-ruminant carcass products with a dominance of dairy products (as suggested by their position between dairy and non-ruminant ellipses). The remaining nine potsherds from this phase plot along the mixing lines between ruminant adipose and non-ruminant adipose products suggesting the mixing of those products.

During the phase III at Ensisheim, all lipid residues plot on the mixing lines. Eight potsherds with $\Delta^{13}C$ values below -3.1 ‰ present lipid profiles dominated by dairy residues but their shift from the reference ellipse of dairy products suggest some mixing with non-ruminant carcass products. The remaining eight potsherds ($\Delta^{13}C$ > -3.1 ‰) plot along the mixing line of ruminant and non-ruminant carcass products. No vessel specialisation is visible for this phase.

During phase IV, three potsherds exhibited quite depleted $\Delta^{13}C$ values (ENS-C-5991: -4.5 ‰, ENS-C-5995: -3.6 ‰, ENS-C-6002: -3.9 ‰) corresponding to the mixing of non-ruminant carcass products with a dominance of dairy products. The remaining seven potsherds ($\Delta^{13}C$ > -3.1 ‰) suggest the mixing of ruminant and non-ruminant carcass products.

Vessel specialisation for ruminant product processing was only visible during phase II. Phases III and IV show the mixing of ruminant and non-ruminant products in the same vessel as none of the potsherd fit in the reference ellipses, a dairy signal (mixed with carcass fats, *n* = 18 TLEs) is nonetheless visible during those phases. Interestingly, no TLEs present $\delta^{13}C$ values plotting in the reference ellipse of non-ruminant carcass products, although some mixing is evident, suggesting that pigs only made a minor contribution to the subsistence economy at the site.

5.4.3.3.3 Sierentz

At the site of Sierentz $C_{16:0}$ and $C_{18:0}$ fatty acids display $\delta^{13}C$ values characteristic of ruminant adipose (*n* = 4) and ruminant dairy products (*n* = 3), as well as their mixing with non-ruminant products (*n* = 30; Figure 5-16e, f), a few extracts (*n* = 8) plot quite close to the ruminant adipose ellipses suggesting a dominance of such products and no environmental effect.

During phase IVA, two potsherd extracts plot in the dairy ellipse (SIE-C-5374, SIE-C-5426), and one in the ruminant adipose ellipse (SIE-C-5401) suggesting some vessel specialisation for

ruminant products. A total of nine sherds shifted from the reference ellipses of dairy products exhibit $\Delta^{13}C$ values below -3.1 ‰ suggesting a dominance of dairy mixed with non-ruminant carcass products and the remaining ten, plot along the mixing line of ruminant and non-ruminant carcass products.

During the phase IVB, one sherd (SIE-C-5363) corresponds to dairy products and three (SIE-C-5342, SIE-C-5411, SIE-C-5443) to ruminant adipose products. A total of 11 potsherds plot along the mixing lines suggesting the mixing of ruminant and non-ruminant carcass products. The remaining six sherds with $\Delta^{13}C$ values below -3.1 ‰ suggest the mixing of non-ruminant carcass products with a dominance of dairy products.

Some vessel specialisation for ruminant products is visible during the two LBK phases at the site with a total of 3 vessels being use for dairy products and 4 being used for ruminant carcass products. However, there are no TLE profiles with $\delta^{13}C$ values which suggest the processing of non-ruminant carcass products, although some mixing is evident, suggesting that pigs only made a minor contribution to the subsistence economy at the site. A clear dairy signal (mixed with carcass fats, $n = 18$ lipid residues) is nonetheless visible during those phases.

The two sites of Sierentz and Ensisheim showed similar features with an economy relying both on carcass and dairy products, as opposed to Colmar where evidence for dairying is limited but this could be due to the low lipid recovery at this site. None of the sites comprise $\delta^{13}C$ values suggesting the use of freshwater resources from adjacent river or stream (Cramp and Evershed 2014). Based on $\delta^{13}C$ analyses the potsherds with animal fats from both sites are good candidates for CSRA despite mixing between ruminant and non-ruminant products in a majority of the potsherds.

5.4.3.4 Comparison with archaeozoological data

The faunal assemblage in the UA is dominated by domesticated animals (Appendix 6-7) with ~ 3,500 remains discovered at Colmar (mainly from the Early LBK phase; Arbogast 1993), and ~ 6,000 remains recovered at Ensisheim (Arbogast 1992). Unfortunately, due to the acidity of the soil at the site of Sierentz few faunal remains survive, and no bones identification was performed at the site (Wolf 1999). One fish bone and 4 shell fragments support the limited use of aquatic resources at Colmar. The UA economy showed a dominance of domesticated animals corresponding to 90.5 % of the number of faunal remains (NISP) at Colmar. At Ensisheim the domesticated animals correspond to 94.2 %, 96.1 % and 88.3 % NISP for the Early, Middle and Late LBK, respectively.

The $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ FAs showed the presence of ruminant and non-ruminant products which correspond, according to the archaeozoological studies, to cattle, sheep, goat and pig. As previously, by weighting the faunal remains for the meat available per animal, these can be compared to the lipid residues present in pottery vessels (O'Connor 1991; Figure 5-17, Section 5.4.1.4). There are overall more carcass products available from cattle than caprines and pigs. Compared with the LA groups, the faunal assemblage comprises significantly fewer pigs (ca. 10 % of the meat weight), which is a general pattern in the UA compared to LA during the Late and Middle LBK (Jeunesse 1995).

5.4.3.4.1 Colmar

For the Early LBK phase at Colmar (the only phase with significant faunal remains; Figure 5-17a), there is a good correlation between the weighted number of pig remains (10 %) and the proportion of non-ruminant products in pottery vessels (12 %). The remaining TLEs present FAs $\delta^{13}C$ values which correspond to the mixing of non-ruminant with ruminant carcass

products (76 %) or with dairy products (12 %). The cattle comprise 80 % of the meat weight and caprine 5 %, therefore, the use of carcass products of the ruminant animals is likely underestimated in the potsherds due to the $\delta^{13}C$ values of FAs showing mixing of different animal products.

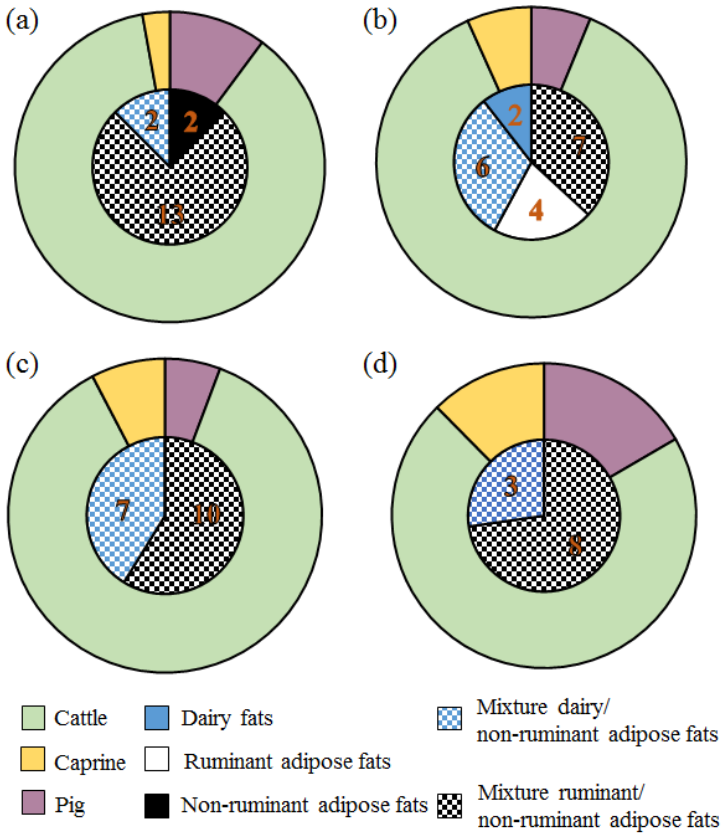

Figure 5-17: The outer circle is the meat weight percentage of domesticated animals and the inner circle is the percentage of animal products recovered in potsherds based on $\delta^{13}C$ values of FAs at Colmar (a) Early LBK, and Ensisheim (b) Early LBK, (c) Middle LBK and (d) Late LBK. The animal remains have been weighted with the availability of meat per animal, cattle =7.33, pig =3.33, sheep/goat = 1 (O'Connor 1991).

5.4.3.4.2 Ensisheim

Interestingly, during the Early and Middle LBK phases at Ensisheim (Figure 5-17b, c, d) the meat yields are similar, corresponding to 6 % for pigs, 87 % for cattle and 7 % for caprine, suggesting animal management did not change throughout these two phases.

The Early phase at Ensisheim (Figure 5-17b) comprised 21 % of ruminant carcass product lipid residues, which is likely considerably underestimated compared to the carcass products available from ruminant animals (94%). This is probably due to the mixing of non-ruminant and ruminant adipose products (37 %). Dairy products comprise 11 % of the $\delta^{13}C$ values of FAs and a further 32 % of dairy residues are mixed with non-ruminant products. Interestingly, only in this phase did ruminant carcass and dairy lipids plot in the reference ellipses, suggesting some vessel specialisation.

During the Middle phase (Figure 5-17c), the FAs $\delta^{13}C$ values indicate the mixing of non-ruminant products with ruminant adipose (59 %) and dairy (41 %) products. No correlation with the availability of carcass products from the different species can be seen but the $\delta^{13}C$ values evidence demonstrates extensive use of the dairy products at the site. For both Early and Middle LBK phases the proportion of pig carcass product availability was low (6 %) and no FAs $\delta^{13}C$ values plotted within the reference ellipse of non-ruminant adipose products.

During the Late LBK (Figure 5-17d) the pig remains constitute 17 % of the carcass products available but this is not shown by the ORA analysis as none of the potsherds plot in the non-ruminant reference ellipses, suggesting mixing or processing of pig without the use of pots. During this phase, cattle and caprine meat weights were estimated to be 71 % and 12 % of the carcass products available, respectively. There were no FA $\delta^{13}C$ values within the reference ellipse of non-ruminant adipose products. However, a total of 73 % of the $\delta^{13}C$ values suggest mixing between ruminant and non-ruminant adipose products. A total of 27 % of the $\delta^{13}C$ values comprised dairy mixed with non-ruminant products, supporting the processing of dairy products.

Dairy processing makes a significant contribution to the economy at the site of Ensisheim. However, for the Late phase, compared with the Early/Middle phase, there are fewer lipid residues showing a dominance of dairy products (27 % against ca. 40 %) and an increased proportion of pig remains (17 % against 6 %). This could suggest a decrease in dairy production and an increase in consumption of porcine carcass products. There is certainly clear evidence of mixing between (mainly) dairy but also some ruminant carcass and non-ruminant products (see Figure 5-18), however, no lipid profiles plotted solely within the reference ellipse for non-ruminant product processing. This suggests that vessels no longer had specialised uses (as in the previous phase) and also that dairying became less important. Based on $\delta^{13}C$ values compared with faunal remains, the potsherds containing animal fats are good candidates for CSRA.

5.4.4 Discussion of dietary practices and vessel use in the Alsace

5.4.4.1 Spatial and temporal disparity of dietary practices in Alsace

The comparison of lipid residue profiles from LBK groups (all phases) in the Lower and Upper Alsace regions shows a significant difference between the dietary and animal management practices (Figure 5-18). The exploitation of both carcass (ca. 60 % of lipid residues or n = 72 potsherds) and dairy (ca. 40 % or n = 33 potsherds) products by the groups in the UA region is evident from the Early LBK phase, whereas, in LA, limited evidence existed for dairying (ca. 5 % or n = 4 potsherds) is seen mainly during the LBK IVa1 phase at Bischoffsheim. Thus, the subsistence economy of LA groups appears to mainly rely on carcass products (ca. 95 % or n = 63 potsherds) although it should be noted that dairy products could have been processed in containers other than potsherds (e.g. baskets or wooden bowls), which have not survived. The strong dairy signal (ca. 40 %) in UA groups is not entirely recovered at the border site of

Colmar (12 % or *n* = 2 potsherds) and the use of non-ruminant products (in reference ellipses 12 % or *n* = 2 potsherds) appears similar to the LA. These results could be interpreted as a mixed influence at the site of Colmar of the two regional LBK groups, with one exploiting dairy and the other one pig products, although the poor lipid preservation may mean that the lipid residues recovered (in *n* = 17 potsherds) are not representative of procurement and processing practices at the site. One noticeable difference in the faunal remains corresponds to the availability of pig carcass products. In the LA, the pigs contribute significantly to the diet (ca. 20 % or *n* = 17 potsherds in reference ellipses) and represent ca. 30 % of the meat yield. In contrast, in the UA, the pigs represent ca. 10 % of the meat yield and a significant use of dairy products (ca. 40 %) as opposed to non-ruminant products is visible (0 % of TLEs plot within non-ruminant ellipse). These results support different herd management strategies for the two LBK groups, related to the products targeted from the animals.

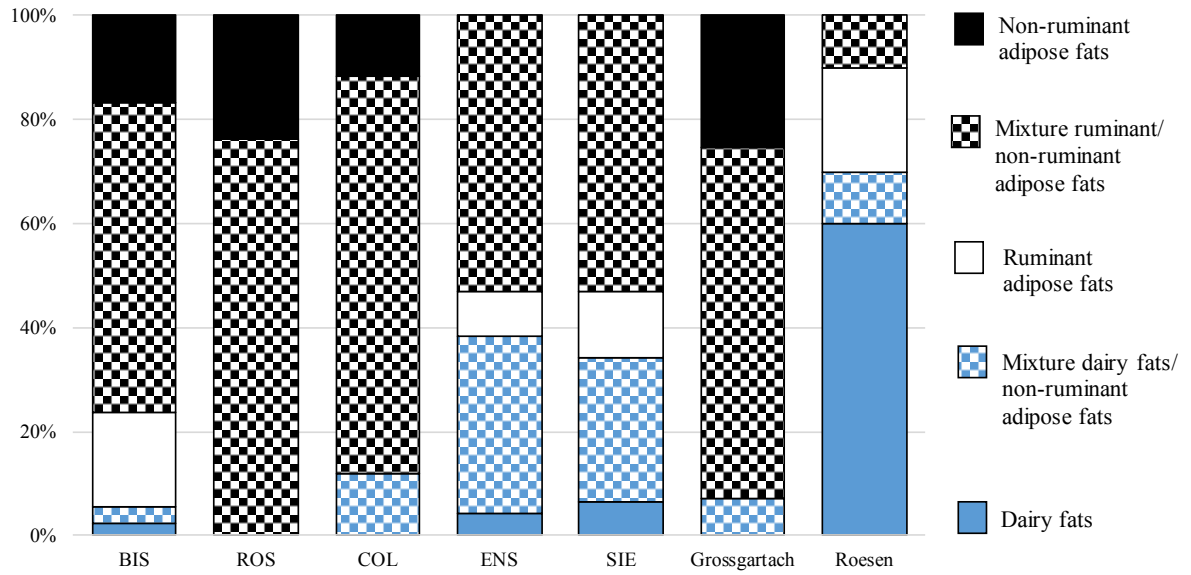

Figure 5-18: Relative proportion of animal products residues recovered in potsherds at the Alsatian sites.

Organic residue analysis of the pottery assemblages from the different cultural traditions present in the LA and UA (Jeunesse 1995) confirms the differing subsistence strategies/animal

management practices of these groups, i.e. dairying. It is known that the LA groups arrived in the region from the Neckar valley and ultimately remained in the region, whereas the UA groups likely originated from the Danuban region and subsequently migrated from Upper Alsace to the Paris Basin. Thus, further insight on the origins/evolution of their differing subsistence strategies (Jeunesse 1995; Arbogast and Jeunesse 2013) may be provided by a wider scale study of LBK groups (see Chapter 6).

In the Lower Alsace there is a significant shift of dietary practices between the LBK and the Grossgartach cultural groups to the Roessen in the LA (Figure 5-18). The LBK in LA is a cattle-based culture leaving a significant amount of porcine faunal remains (ca. 30 % weighted NR), shown by FAs $\delta^{13}C$ values to have been widely processed in pots (ca. 20 % of the lipid residues). The Grossgartach left fewer pig remains (ca. 12 % weighted NR) in the faunal assemblage, however, non-ruminant carcass products were widely recovered in potsherds (ca. 25 % of the pottery animal product residues). The ORA suggested an economy relying mainly on carcass products. Interestingly, sieves are common for the Grossgartach culture in the region (although none were found at the site of Rosheim) and could be evidence for more intense dairying practices for cheese making by this culture (Denaire 2009a, 2013; Salque *et al.* 2013) but this would require ORA of sieves.

The culture of Roessen showed clear evidence for an economy based on dairy products (ca. 65 % of the lipid residues) with some exploitation of ruminant carcass products. It is possible that the decrease in herd size from the Grossgartach (~75 % fewer remains) reflect the shift to an economy based mainly on secondary products, such as milk, where animals were kept alive instead of being killed for their meat (Sherratt 1983; Vigne and Helmer 2007). This regional variation shows similarities to the site of Kopydłowo in Poland, which revealed limited evidence for dairying in sieves during the LBK and the next cultural group (Late Band

Pottery Culture) before a wider adoption of dairying by the Middle Neolithic group of the Funnel(-neck-)beaker culture (Roffet-Salque and Evershed 2015).

Evidence of plants processing was recovered from the site of Bischoffsheim in only three potsherds, while the use of beeswax in pottery vessels was widely identified from the Early LBK phases and beyond in both the LA and UA region. The presence of beeswax in pottery vessels was also discovered during the Middle Neolithic period. This suggests the widespread use of bee products by prehistoric farmers in the region, as previously identified in other parts of Europe and the Near East during the late Holocene (Roffet-Salque *et al.* 2015).

Despite settlements lying in close proximity to rivers, lipid residue analysis of the potsherds, in combination with the faunal remains, suggests no significant contribution of aquatic resources to the diet (and thus reservoir effect) of the cultural groups in the region. This supports the farming economy of the Neolithic groups in the region as opposed to hunting and fishing and makes these lipid residues excellent candidates for CSRA dating.

5.4.4.2 Vessel specialisation and suitability for ^{14}C dating

As previously discussed, the sherds suitable for radiocarbon dating must contain high a concentration of lipids ideally comprising animal FAs (terrestrial) rather than profiles 'mixed' with plants or beeswax, to avoid dating more than one source of C. A summary of sherds analysed which meet these criteria is given in Table 5-1. Thus, a total of 90 sherds, i.e. 10 % of the total of sherds analysed, were regarded as suitable for ^{14}C dating, if sherd size allows. The proportion of sherds available from each site in assemblage varies considerably, with 6 % coming from the LBK in the UA, 11 % from the LBK in LA and 26 % from Middle Neolithic groups. This suggests that more sherds suitable for CSRA come from younger deposits, perhaps reflecting factors relating to preservation. However, for relatively contemporaneous sites, the

assemblages showed significant variation (the UA average was lowered by the poor preservation at Colmar). Therefore, this suggests that preservation conditions at sites must be considered when selecting suitable materials for dating from older assemblages.

Table 5-1: Number of sherds analysed, of sherds with animal products, of sherds with concentration > 500 µg.g^{-1} and of sherds suitable for ^{14}C dating for the overall assemblage, refitted, decorated and undecorated sherds. The percentages are calculated against the total number of sherds in the assemblages. The blue colour corresponds to the LBK in LA, orange to the Middle Neolithic and grey the LBK in UA.

Characteristic	Total sherds		Refitted sherds		Decorated sherds		Undecorated sherds	
	#	%	#	%	#	%	#	%
Number analysed	390	100 %	51	13 %	174	45 %	216	55 %
	86	100 %	26	30 %	21	24 %	65	76 %
	395	100 %	41	10 %	127	32%	268	68 %
Presence of 'pure' animal products	108	28 %	10	26%	22	6 %	86	22 %
	33	38 %	10	12 %	4	5 %	29	34 %
	136	34 %	6	2 %	23	6 %	113	29 %
C^{o} > 500 µg/g	44	11%	1	0.3 %	5	1 %	39	10 %
	29	38 %	7	8 %	4	5 %	25	29 %
	27	7 %	0	0 %	1	0.3 %	26	7 %
Suitability for ^{14}C dating	43	11 %	1	0.3 %	5	1 %	38	10 %
	22	26 %	7	8 %	1	1 %	21	24 %
	25	6 %	0	0 %	0	0 %	25	6 %

Overall, the suitability, i.e. high FA concentrations, of undecorated sherds for dating has been shown to be better than those of decorated pottery vessels, i.e. 84 undecorated potsherds against 6 decorated potsherds. The highest concentrations of animal products with 'pure' profiles were mainly recovered from undecorated pottery vessels (Figure 5-19). Conversely, decorated vessels showed, on average, lower lipid concentrations. The residues extracted from decorated vessels often showed mixed profiles comprising animal products and plant/beeswax lipid signals, whereas, the undecorated sherds showed mainly 'pure' animal product FA profiles, or, no residues. This difference supports interpretation relating to vessel specialisation during the LBK with undecorated vessels being used as cooking pots and the decorated vessels being used as table dishes. The same distinction is visible for the Middle Neolithic groups. Thus, the potsherds used as cooking vessels (undecorated) are better candidates for radiocarbon analysis.

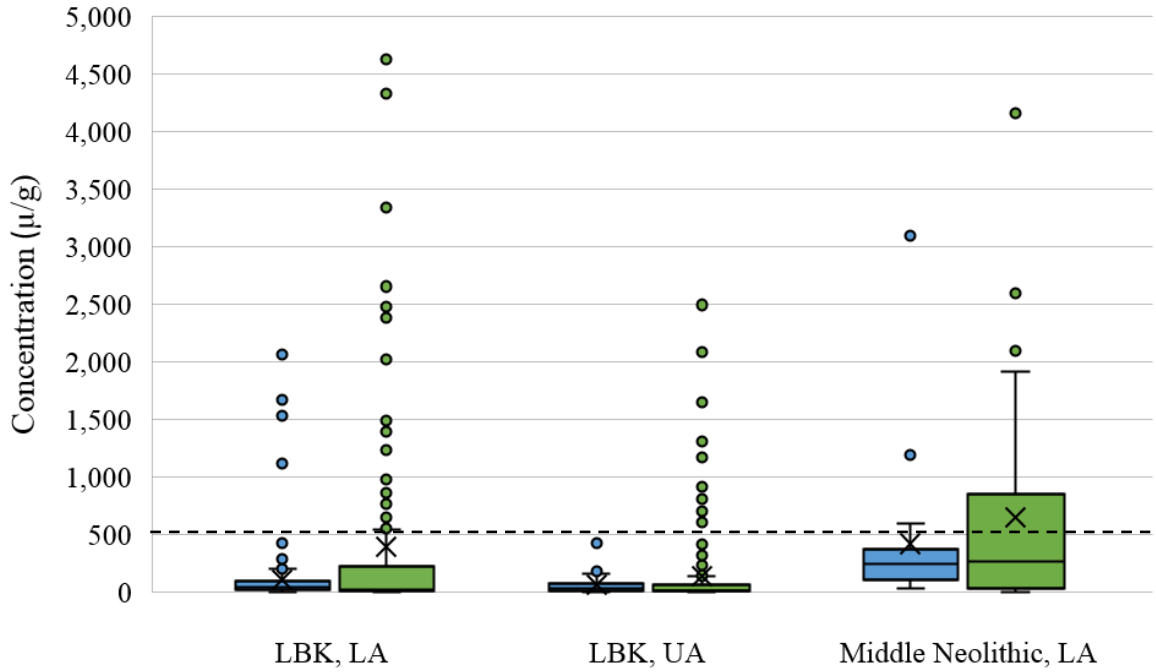

Figure 5-19: Box and whisker plot of lipid concentration in decorated potsherds (blue) and undecorated potsherds (green). The dashed line corresponds to the lowest limit of lipid concentration for ^{14}C dating.

The number of refitted sherds suitable for dating represents less than 1 % of the total assemblage. Refitting criteria does not influence the suitability for dating based on the lipid profile and concentration, but it influences on the selection materials that are not intrusive or residual. The lipid recovery rate and thus suitability for radiocarbon dating would be related to the refitted pot function, i.e. serving dish or cooking vessel, and thus to the decorated or undecorated style in this case. The sampling was not equal for the single/refitted sherds due to a lower occurrence of the refitted sherds in the studied contexts, explaining the low suitability for ^{14}C dating of such potsherds.

The above results showed that only 6 to 26 % of sherds in the assemblages contained sufficient lipid (FA) suitable for radiocarbon dating. This suggests that a pottery assemblage of approximatively 5 to 10 times the number of sherds required to be radiocarbon dated must be analysed by ORA in order to provide candidate sherds for a dating programme.

5.5 Radiocarbon dating of pottery vessels from Lower Alsace

5.5.1 The *Linearbandkeramik*

5.5.1.1 CSRA determinations

Organic residue analysis of pottery vessels revealed that 11 % (n = 31) of the assemblage for Bischoffsheim and 13 % (n = 13) for Rosheim comprised animal fats product profiles containing suitable concentration of FA for ^{14}C dating. However, a few sherds were too small in size to allow a second sampling. Thus, a total of 19 pottery vessels (16 from Bischoffsheim and 3 from Rosheim), from phases IIB to IVb, were selected for radiocarbon dating (Table 5-2). Phase IIC did not contain pottery vessels matching the criteria discussed previously, and thus none were sampled.

A total of 16 pairs of ^{14}C measurements on $C_{16:0}$ and $C_{18:0}$ FAs successfully passed the internal quality control on the two FAs, six failed, and four generated only one target. An uneven lipid distribution in the clay (Charters *et al.* 1993b) may have affected the last four potsherds as less C was extracted than the initial lipid residue results predicted. The first extraction of 3 pottery vessels (BIS-C-4002, BIS-C-5244, BIS-C-4063) failed the internal control, suggesting either contamination during extraction or isolation. In all cases, a second extraction and isolation yielded results identical within error. The second extract on potsherd BIS-C-4063 which was isolated 3 times in the PCGC (in random order) also showed a good reproducibility as all measurements passed the χ^2 test at 5 % level (T' = 2.3, T'(5%) = 11.1, υ = 5). Lipids from potsherd ROS-C-4695 were extracted twice and passed the internal criteria each time. In total, the measurements passed the χ^2 test at 5 % level (T' = 2.3, T'(5%) = 7.8, υ = 3). The last two examples support the reproducibility of the method (i) starting with the extraction of lipids from the clay and (ii) the PCGC isolation, giving similar ^{14}C dates in all cases.

Table 5-2: CSRA dating of pottery vessels from the sites of Bischoffsheim and Rosheim.

Sample	BRAMS #	Phase	Pit	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range
BISC3994-$C_{16:0}$	1245.3.1	IIB	1413	81	0.4615 ± 0.0030	6,212 ± 55	•
BISC3994-$C_{18:0}$	1245.3.2	IIB	1413	121	0.4650 ± 0.0029	6,151 ± 53	
BISC4002- $C_{16:0}$	1248.1.1	IIB	1413	274	0.4613 ± 0.0027	6,174 ± 42	X
BISC4002-$C_{18:0}$	1248.1.2	IIB	1413	324	0.4650 ± 0.0025	6,267 ± 41	
BISC4002- $C_{16:0}$	1248.3.1	IIB	1413	154	0.4613 ± 0.0027	6,215 ± 51	•
BISC4002-$C_{18:0}$	1248.3.2	IIB	1413	242	0.4600 ± 0.0025	6,237 ± 45	
BISC5203-$C_{16:0}C_{18:0}$	1257.1.1	IIB	1193	122	0.4635 ± 0.0030	6,182 ± 54	-
BISC4504-$C_{16:0}$	1249.1.1	III	375	130	0.4704 ± 0.0027	6,058 ± 48	X
BISC4504-$C_{18:0}$	1249.1.2	III	375	209	0.4585 ± 0.0024	6,264 ± 44	
BISC4505-$C_{16:0}$	1255.1.1	III	375	94	0.4670 ± 0.0031	6,118 ± 56	•
BISC4505-$C_{18:0}$	1255.1.2	III	375	125	0.4657 ± 0.0031	6,138 ± 56	
BISC5242- $C_{16:0}$	1253.1.1	III	138	291	0.4612 ± 0.0023	6,207 ± 42	•
BISC5242-$C_{18:0}$	1253.1.2	III	138	215	0.4639 ± 0.0024	6,170 ± 43	
BISC5244- $C_{16:0}$	1252.1.1	III	138	199	0.4659 ± 0.0024	6,136 ± 44	X
BISC5244-$C_{18:0}$	1252.1.2	III	138	715	0.4537 ± 0.0022	6,349 ± 40	
BISC5244-$C_{18:0}$	1252.2.2	III	138	2138	0.4636 ± 0.0027	6,176 ± 50	
BISC5288-$C_{16:0}$	1247.1.1	III	1735	161	0.5054 ± 0.0026	5,482 ± 44	X
BISC5288-$C_{18:0}$	1247.1.2	III	1735	275	0.4670 ± 0.0023	6,117 ± 42	
BISC4529-$C_{16:0}$	1209.1.1	IVa1	538	285	0.4635 ± 0.0017	6,177 ± 31	•
BISC4529-$C_{18:0}$	1209.1.2	IVa1	538	386	0.4678 ± 0.0017	6,103 ± 30	
BISC4519-$C_{16:0}$	1221.1.1	IVa1	538	265	0.4574 ± 0.0017	6,284 ± 32	X
BISC4519-$C_{18:0}$	1221.1.2	IVa1	538	315	0.4678 ± 0.0017	6,102 ± 31	
BISC4531-$C_{16:0}$	1267.1.1	IVa1	538	195	0.4618 ± 0.0023	6,185 ± 57	•
BISC4531-$C_{18:0}$	1267.1.2	IVa1	538	108	0.4639 ± 0.0024	6,112 ± 44	
BISC4549-$C_{16:0}C_{18:0}$	1254.1.1	IVa2	265	281	0.4604 ± 0.0020	6,236 ± 37	-
BISC4549-$C_{16:0}$	1254.2.1	IVa2	265	308	0.4575 ± 0.0020	6,282 ± 37	•
BISC4549-$C_{18:0}$	1254.2.2	IVa2	265	372	0.4557 ± 0.0019	6,313 ± 36	
BISC4546-$C_{16:0}C_{18:0}$	1250.1.1	IVa2	265	370	0.4594 ± 0.0026	6,247 ± 40	-
BISC4063-$C_{16:0}$	1211.1.1	IVb	941	279	0.4656 ± 0.0017	6,141 ± 31	X
BISC4063-$C_{18:0}$	1211.1.2	IVb	941	289	0.4616 ± 0.0017	6,211 ± 31	
BISC4063-$C_{16:0}$	1211.2.1	IVb	941	193	0.4607 ± 0.0025	6,226 ± 47	•
BISC4063-$C_{18:0}$	1211.2.2	IVb	941	212	0.4616 ± 0.0025	6,210 ± 46	
BISC4063-$C_{16:0}$	1211.3.1	IVb	941	154	0.4639 ± 0.0026	6,171 ± 48	•
BISC4063-$C_{18:0}$	1211.3.2	IVb	941	248	0.4608 ± 0.0024	6,223 ± 45	
BISC4063-$C_{16:0}$	1211.4.1	IVb	941	186	0.4581 ± 0.0026	6,271 ± 48	•
BISC4063-$C_{18:0}$	1211.4.2	IVb	941	277	0.4608 ± 0.0024	6,224 ± 44	
BISC5265-$C_{16:0}$	1246.1.1	IVb	940	163	0.4634 ± 0.0024	6,179 ± 44	•
BISC5265-$C_{18:0}$	1246.1.2	IVb	940	259	0.4604 ± 0.0023	6,230 ± 42	
BISC4568-$C_{16:0}$	1256.1.1	IVb	941	416	0.4587 ± 0.0020	6,261 ± 36	•
BISC4568-$C_{18:0}$	1256.1.2	IVb	941	351	0.4641 ± 0.0018	6,171 ± 35	
ROSC4678-$C_{16:0}$	1145.2.1	IVb	3009	284	0.4654 ± 0.0017	6,144 ± 31	•
ROSC4678-$C_{18:0}$	1145.2.2	IVb	3009	244	0.4641 ± 0.0018	6,167 ± 30	
ROSC4695-$C_{16:0}$	1208.1.1	IVb	3011	345	0.4654 ± 0.0018	6,144 ± 31	•
ROSC4695-$C_{18:0}$	1208.1.2	IVb	3011	325	0.4686 ± 0.0017	6,088 ± 31	
ROSC4695-$C_{16:0}$	1208.2.1	IVb	3011	301	0.4663 ± 0.0017	6,128 ± 31	•
ROSC4695-$C_{18:0}$	1208.2.2	IVb	3011	267	0.4653 ± 0.0011	6,147 ± 31	
ROSC4694-$C_{16:0}$	1210.1.1	IVb	3011	214	0.4649 ± 0.0018	6,153 ± 33	•
ROSC4694-$C_{18:0}$	1210.1.2	IVb	3011	169	1.4654 ± 0.0019	6,144 ± 34	

• $C_{16:0}$ and $C_{18:0}$ FAs identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ FAs identical within 2σ
X $C_{16:0}$ and $C_{18:0}$ FAs non-identical within 2σ

5.5.1.2 Comparison with reference radiocarbon dates

Ten of the potsherds selected for dating came from features included in the original seriation (Denaire *et al.* 2017) and the remaining five originated from additional features. An updated seriation was created to integrate the new features (Figure 5-20; Appendix 6-17; Courtesy of A. Bayliss and A. Denaire).

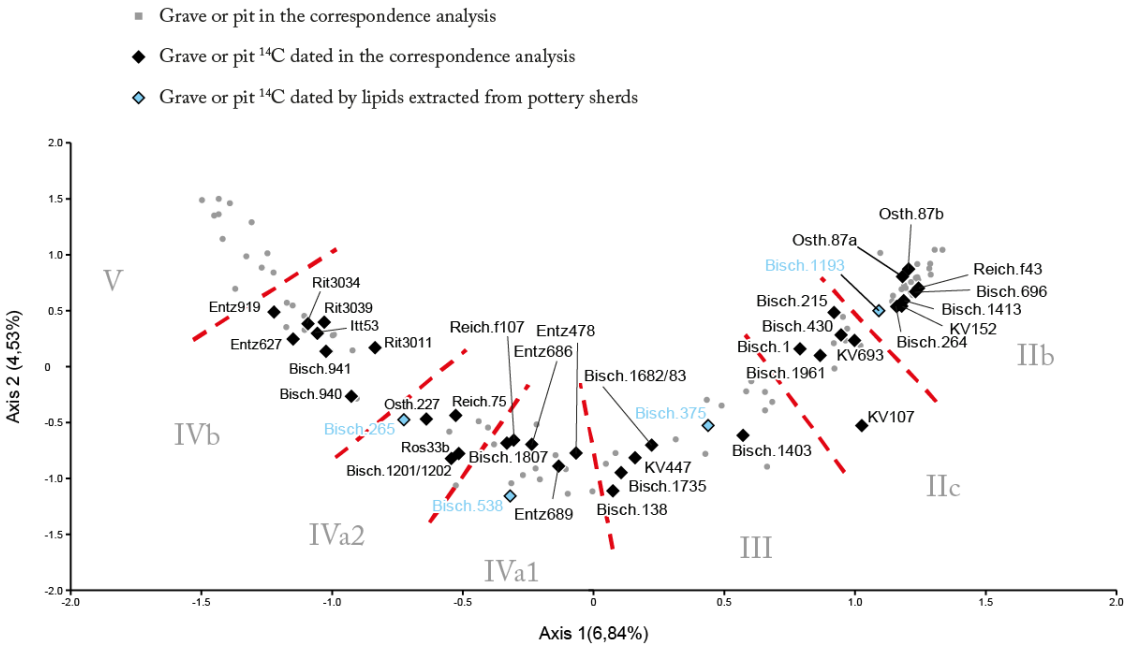

Figure 5-20: Revised correspondence analysis of LBK ceramics in the Lower Alsace. Courtesy of A. Bayliss and A. Denaire.

The pit 3009 from Rosheim "Rittergass" could not be included as the pottery assemblage included only one of the decorative motifs in the seriation. The other pit 3011 of the same house was, however, clearly in phase IVb. At Bischoffsheim, pit 1193 was dated to phase IIB, pit 375 to phase III, pit 538 to phase IVa1 and pit 265 to phase IVa2. In the revised seriation, two features were placed in different phases to their original phase. Pit Reich.107 was mistakenly placed in IVa2 in the original model and is now in phase IVa1. The unique charcoal date of the feature provides a *terminus post quem* for the deposition, and thus the change would make no significant difference to the original model. Pit Bisch.1735 is now dated to phase III but was

originally dated to IVa1 due to a typographical error in the coding of one decorative motif. The uncalibrated ^{14}C measurements of lipid residues and reference dates from the sites of Bischoffsheim and Rosheim (Denaire *et al.* 2017; Appendix 6-18) were first compared by phase.

5.5.1.2.1 LBK IIB

A total of three pottery vessels (BIS-C-3994, BIS-C-4002 and BIS-C-5203) from phase IIB were dated. Dates on the $C_{16:0}$ and $C_{18:0}$ FAs from potsherd BIS-C-3994 were combined to give a date of 6,180 ± 39 BP, likewise the FAs from BIS-C-4002 were combined to give a date of 6,227 ± 35 BP, while BIS-C-5203 was dated by one target to 6,182 ± 54 BP. Three measurements, two on animal bones and one on a visible residue, from phase IIB at Bischoffsheim were dated to 6,257 ± 33 BP (SUERC-47710), 6,225 ± 40 BP (OxA-2965) and 6,207 ± 34 BP (SUERC-55324; Denaire *et al.* 2017). In summary, the collagen and lipid extracts showed statistically consistent ^{14}C measurements (T' = 3.0, T'(5%) = 9.2, υ = 5).

5.5.1.2.2 LBK III

A total of five pottery vessels from phase III were dated, two passed the internal quality control but the remainder failed it. The potsherd BIS-C-5244 was sampled a second time but could only generate one target dated at 6,176 ± 50 BP. The dates on both FAs from potsherd BIS-C-4505 were combined to give a date of 6,128 ± 41 BP, and from BIS-C-5242 the FAs were combined to give a date of 6,189 ± 32 BP. A total of 5 animal bones (one from pit Bisch.1735) and two visible residues were dated at Bischoffsheim giving radiocarbon ages ranging between 6,252 ± 38 BP (OxA-30786) and 6,161 ± 36 BP (OxA-27772; Denaire *et al.* 2017). The two sherds which passed the internal criterion and the single target showed statistically consistent results with the reference measurements (T' = 8.0, T'(5%) = 16.9, υ = 9).

5.5.1.2.3 LBK IVa1

A total of four pottery vessels from the phase IVa1 were dated, two passed the internal quality control, and two failed. The radiocarbon dates on both FAs from potsherd BIS-C-4529 were combined to give a date of 6,139 ± 25 BP, and BIS-C-4531 FAs were combined to give a date of 6,138 ± 36 BP. One date on animal bone collagen from the phase IVa1 at Bischoffsheim was duplicated but showed measurements not identical within error (OxA-2773: 6,219 ± 34 BP; SUERC-46499: 6,337 ± 34 BP) and was treated as residual in the model (Denaire *et al.* 2017). The uncalibrated dates can therefore not be compared for this phase.

5.5.1.2.4 LBK IVa2

Two pottery vessels from the phase IVa2 were dated. One passed the internal quality control (BIS-C-4549) and the two FA dates combined to give a date of 6,298 ± 28 BP, whereas the other generated only one target dated to 6,247 ± 40 BP. One animal bone date is available at Bischoffsheim dated to 6,219 ± 34 BP (SUERC-46498; Denaire *et al.* 2017). All together the collagen and lipid dates are statistically consistent (T' = 3.4, T'(5%) = 6.0, υ = 2).

5.5.1.2.5 LBK IVb

Three pottery vessels from Bischoffsheim and three pottery vessels from Rosheim were dated for the phase IVb. At Bischoffsheim all the sherds passed the internal quality control. The ^{14}C dates on both FAs from potsherd BIS-C-4063 were combined to give a date of 6,221 ± 26 BP, from BIS-C-5265 to give a date of 6,206 ± 33 BP and from BIS-C-4568 to give a date of 6,214 ± 28 BP. Three animal bones dates are available but, one (SUERC-46509: 6,084 ± 34 BP) showed poor agreement with the model as its age is too recent (A: 19; Denaire *et al.* 2017) and is not considered here. The other animal bones are dated from 6,172 ± 32 BP

(OxA-27776) and 6,156 ± 34 BP (SUERC-46510; Denaire *et al.* 2017). All together the collagen and lipid dates are statistically consistent (T' = 3.4, T'(5%) = 9.5, υ = 4).

At Rosheim all the potsherds passed the internal quality control. The ^{14}C on both FAs from potsherd ROS-C-4678 were combined to give a date of 6,155 ± 26 BP, ROS-C-4695 to give a date of 6,127 ± 23 BP and ROS-C-4694 to give a date of 6,149 ± 34 BP. A total of six ^{14}C measurements on animal bones are available, giving dates ranging from 6,222 ± 31 BP (OxA-27808) and 6,174 ± 34 BP (SUERC-46512), one of which was deemed as residual (OxA-27809: 6,274 ± 31 BP; Denaire *et al.* 2017) and not considered here. Altogether the collagen and lipid dates are statistically consistent (T' = 11.1, T'(5%) = 15.5, υ = 8).

5.5.1.3 Evaluation with Bayesian statistical model

The original model based on ^{14}C-dated articulated bones and visible residues was published in Denaire *et al.* (2017). However, this required re-evaluation (due errors in the seriation chronology of two LBK contexts in the original seriation study; Section 5.5.1.2), prior to being able to integrate the new radiocarbon dates of lipids from pottery vessels. At the time of writing this thesis, the revised reference statistical model was not ready. The model including the dates on pottery vessels being only valid if the model without those dates is valid, (i.e. the relative chronology based on seriation and typological sequence together with radiocarbon dates on animal bone give results that could be used as reference), the evaluation of the accuracy of the CSRA measurements could unfortunately not be performed in the Bayesian statistical model.

5.5.1.4 Discussion

The 19 vessels from the LBK sequence subject of this chapter constitutes the largest number of pottery vessels dated from their absorbed residues from a single regional chronology. Most

of them successfully passed the internal criterion of the two FAs demonstrating consistent individual measurements, providing FA dates for potsherds dated to ca. 6,200 BP. However, four potsherds had no internal control on the FAs, highlighting the fact the inhomogeneity of lipids distribution in a potsherd (Charters *et al.* 1993b) which may affect the suitability of sherds for ^{14}C dating despite extensive ORA pre-screening. Even though the ^{14}C dates could not be evaluated within a Bayesian framework the uncalibrated measurements on lipids extracted from pottery vessels are in good agreement with the previously published (Denaire *et al.* 2017) uncalibrated radiocarbon measurements from bone collagen and visible residues for the same phases of the LBK at the sites of Bischoffsheim "AFUA du stade" and Rosheim "Rittergass". The precise relative chronology of the LBK ceramic sequence and the statistical modelling may, however, reveal some of the potsherds to be residual or intrusive despite successfully passing the χ^2 test at the 5 % level with the reference measurements. For example, this could be the case with potsherd BIS-C-4529 from the phase IVa2 which shows the oldest uncalibrated CSRA date on a pottery vessel from the site of Bischoffsheim despite its late position in the seriation. Evaluation of the accuracy of compound-specific radiocarbon dates on the lipids extracted from pottery vessels now requires rigorous testing using the Bayesian statistical framework.

5.5.2 The Middle Neolithic

5.5.2.1 CSRA determinations

Among the Grossgartach pottery assemblage, 15 sherds (26 %) showed suitable concentration for ^{14}C dating. For the Roessen 7 sherds (24 %) from the assemblage were suitable. A total of six potsherds (3 refitted) from the Grossgartach and two from the Roessen cultures (Table 5-3) were selected for radiocarbon dating.

A total of 4 sherds successfully passed the internal quality control, three sherds presented only one target, and one failed the internal criterion. Potsherd ROS-C-4649 failed the internal control, however, another measurement on the same potsherd with the $C_{16:0}$ and $C_{18:0}$ FAs combined in the same trap (BRAMS-1528.1.1) yielded a date consistent within a 2σ range of the one $C_{18:0}$ only (BRAMS-1534.1.2), suggesting that the $C_{16:0}$ target was contaminated with more 'modern' C during the isolation of the FA. The sherd ROS-C-4657 was dated on both individual and combined FAs, with all the measurements passing the χ^2 test at the 5 % level (T' = 2.5, T'(5%) = 6.0, υ = 2).

Table 5-3: CSRA dated on pottery vessel from the Grossgartach and Roessen cultures.

Sample	BRAMS #	Group	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range
ROSC4644-$C_{16:0}$	1525.1.1	Grossgartach	195	0.4766 ± 0.0019	5,937 ± 33	•
ROSC4644-$C_{18:0}$	1525.1.2	Grossgartach	508	0.4782 ± 0.0017	5,926 ± 30	
ROSC4648-$C_{16:0}$	1544.1.1	Grossgartach	133	0.4848 ± 0.0022	5,815 ± 39	-
ROSC4649-$C_{16:0}C_{18:0}$	1528.1.1	Grossgartach	151	0.4810 ± 0.0020	5,879 ± 35	-
ROSC4649-$C_{16:0}$	1534.1.1	Grossgartach	170	0.4917 ± 0.0019	5,702 ± 34	X
ROSC4649-$C_{18:0}$	1534.1.2	Grossgartach	153	0.4789 ± 0.0023	5,914 ± 41	
ROSC4657-$C_{16:0}C_{18:0}$	1524.1.1	Grossgartach	213	0.4803 ± 0.0018	5,892 ± 32	-
ROSC4657-$C_{16:0}$	1524.2.1	Grossgartach	134	0.4806 ± 0.0021	5,855 ± 37	••
ROSC4657-$C_{18:0}$	1524.2.2	Grossgartach	153	0.4788 ± 0.0019	5,934 ± 34	
ROSC4596-$C_{16:0}$	1526.1.1	Grossgartach	451	0.4852 ± 0.0017	5,810 ± 30	•
ROSC4596-$C_{18:0}$	1526.1.2	Grossgartach	407	0.4859 ± 0.0017	5,798 ± 30	
ROSC4600-$C_{16:0}$	1527.3.1	Grossgartach	424	0.4799 ± 0.0020	5,897 ± 36	•
ROSC4600-$C_{18:0}$	1527.3.2	Grossgartach	627	0.4792 ± 0.0020	5,909 ± 35	
ROSC4622-$C_{16:0}C_{18:0}$	1529.1.1	Roessen	137	0.4852 ± 0.0024	5,809 ± 32	-
ROSC4629-$C_{16:0}C_{18:0}$	1533.1.1	Roessen	151	0.4880 ± 0.0020	5,763 ± 35	-

• $C_{16:0}$ and $C_{18:0}$ FAs identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ FAs identical within 2σ
X $C_{16:0}$ and $C_{18:0}$ FAs non-identical within 2σ

For the two sherds from the Roessen culture which were dated, the two FAs were combined in the same trap, generating only one target without internal quality control. This suggests once again an uneven lipid distribution in the clay as less C was extracted than predicted. The two ^{14}C measurements gave results identical within error (T' = 0.9, T'(5%) = 3.8, υ = 2).

5.5.2.2 Comparison with reference radiocarbon dates

The pottery vessels from the Grossgartach come from three pits and two of those features were integrated into the correspondence analysis and typological study of the Middle Neolithic (Figure 5-21; Appendix 6-19; Courtesy of A. Denaire and A. Bayliss). The pit 50 at Rosheim "Sandgrube" is assigned to the Grossgartach on typological grounds but as it is a large pit complex (19 m x 11 m) that is not a closed assemblage.

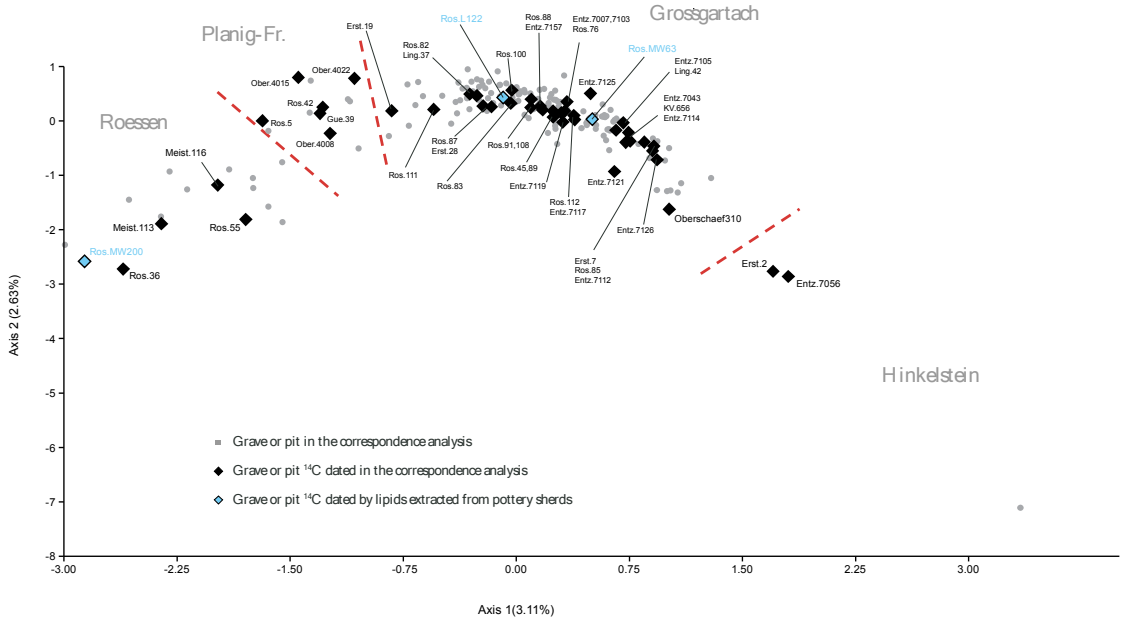

Figure 5-21: Revised correspondence analysis of Middle Neolithic ceramics in Lower Alsace. In blue the features added to the original seriation. Courtesy of A. Bayliss and A. Denaire.

The dating program performed in the region includes ^{14}C dates from the necropolis found at the site Rosheim "Rosenmeer", which correspond to another locality than "Laser, Sandgrube and Mittelweg" at the site of Rosheim which is contemporaneous (Lefranc *et al.* 1999; Appendix 6-18). The uncalibrated ^{14}C measurements on lipid residues and reference dates from Rosheim "Rosenmeer" were compared.

The Grossgartach pottery vessels which passed the internal control were dated on the two FAs from 5,931 ± 26 BP (ROS-C-4644), 5,912 ± 28 BP (ROS-C-4657), 5,804 ± 25 BP (ROS-C-

4596) and 5,904 ± 28 BP (ROS-C-4600). In addition, other potsherds were dated based on one target (both FAs combined in one trap) to 5,815 ± 39 BP (ROS-C-4648), to 5,879 ± 35 BP (ROS-C-4649: BRAMS-1528.1.1 and 5,892 ± 32 BP (ROS-C-4657: BRAMS-1524.1.1). The reference ages from the necropolis range from 5,898 ± 29 BP (OxA-27816) to 5,732 ± 33 BP (SUERC-46276). This range of dates is too broad to show a uniformity with a χ^2 test at the 5 % level, which reflects the long duration of the Grossgartach group as the settlement cannot be divided into subphases (rejected by the model; Denaire *et al.* 2017). Nonetheless, the ^{14}C measurements obtained from the pottery vessels fall in the range of ages obtained from the articulated bones and appear compatible with the Grossgartach group. However, as the potsherds and animal bones do not come from the same contexts a χ^2 test is not possible.

The Roessen pottery vessels were dated by a single target (combining both FAs in a single trap) to 5,809 ± 32 BP (ROS-C-4622) and 5,763 ± 35 BP (ROS-C-4626). The reference measurements range between 5,804 ± 30 BP (OxA-27822) and 5,731 ± 30 BP (SUERC-46445). The dates on lipids extracted from pottery vessels fall in the range of the reference dates and seem compatible with a Roessen settlement but cannot be compared with a χ^2 test as they do not come from the same contexts.

5.5.2.3 Evaluation with Bayesian statistical model

Only the potsherds which passed the internal criterion were included in the Bayesian model for the Middle Neolithic sequence. The part of the model presented in Figure 5-22 is equivalent to Denaire *et al.* (2017), Figure 15, and the second part is identical to that shown in Denaire *et al.* (2017), Figure 16 (Appendix 6-2). The model combining the radiocarbon measurements on potsherds and articulated bones has a good overall agreement (A_{model}: 100). Three pottery lipid dates have good individual agreement (ROS-C-4600, A:98; ROS-C-4596, A:112,

ROS-C-4657, A:90), although the fourth gives poor individual agreement (ROS-C-4644, A:46). This last sherd could be either residual or simply a statistical outlier. The posterior distributions for the six phases boundaries are very similar to those of the original model with their median values varying by an average of 6 years and a maximum of 15 years.

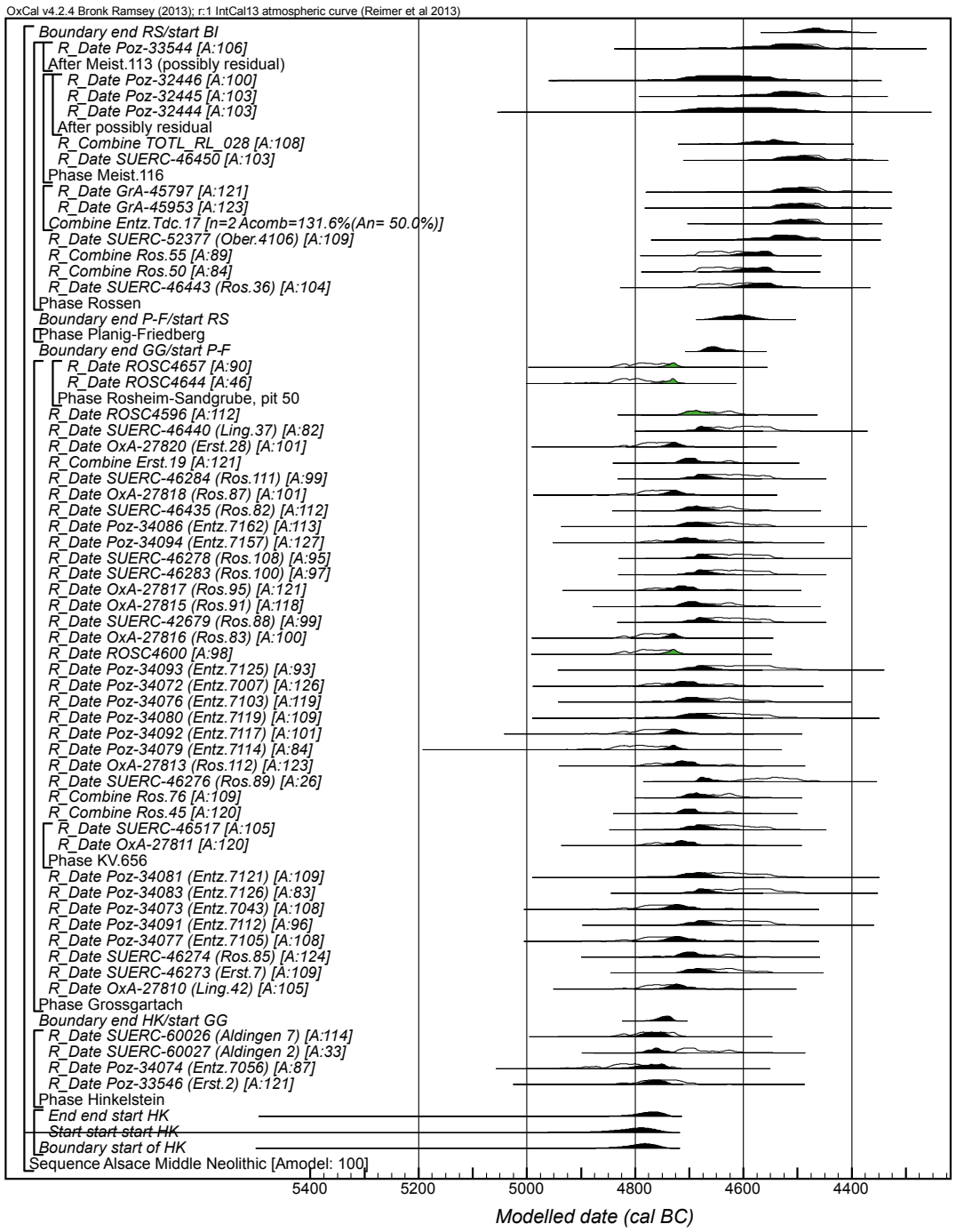

Figure 5-22: Probability distributions of radiocarbon dates from the first part of the sequence of Middle Neolithic ceramics in Lower Alsace suggested by the correspondence analysis including the measurements on absorbed lipids. Format is as Figure 4-10. Courtesy of A. Bayliss (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

5.5.2.4 Discussion

Radiocarbon measurements of lipids extracted from pottery vessels were successfully obtained from the Middle Neolithic culture groups and these results appear compatible with previous dates obtained from the respective cultures. The two potsherds from the Roessen culture were only dated from one target, showing again the possible non-homogeneity of lipid distributions in potsherds (Charters *et al.* 1993b) might affect the amount of lipid C extractable from potsherds despite rigorous pre-screening. The radiocarbon dates on the Grossgartach assemblage were evaluated with a Bayesian statistical model and show a good agreement. Overall, the potsherds fitted well in the Bayesian model, which was prepared from the seriation and typological sequence of pottery assemblages from the Middle Neolithic, and has a similar output to the pre-existing model supporting an accurate dating of the lipids from potsherds ca. 5,900 BP.

5.6 Conclusion

Organic residue analysis of a total of 697 potsherds from sites in the Alsace region demonstrated different subsistence strategies. The LBK group in the LA demonstrated the wide exploitation of carcass products from both ruminant and non-ruminant animals as opposed to milk (5 % of the residues). The LBK in the LA was followed by the Grossgartach culture which showed analogous dietary practices to the LBK, then by the Roessen which showed a reliance on dairy products (65 % of TLEs) and ruminant carcass products. The LBK in Upper Alsace presented in contrast an economy based on both dairy (ca. 40 % of TLEs) and carcass products. The comparison of species profiles from the faunal assemblages to ORA demonstrated the advantages of detecting/ruling out possible reservoir effect by comparing the FAs $\delta^{13}C$ values and faunal remains (i.e. the availability of carcass products from diverse species) at the site.

Interestingly during the LBK, with lower abundance of pig remains, an increasing number of potsherds showing the processing of dairy products was visible supporting different herd managements based on the products targeted from the animal.

The ORA of these pottery assemblages allowed the identification and selection of sherds: (i) with high lipid concentrations, (ii) with a lipid profile which suggested purely animal products were processed, and (iii) those without influence from a reservoir effect. Based on this study, it is estimated that approximatively 10 times the number of sherds required for radiocarbon dating need to be analysed by ORA to detect potsherds containing appropriately high concentrations of lipid. Critically, only pots used as cooking vessels revealed pure FAs profiles and the high lipid concentration required for dating. This was emphasised by the low lipid concentrations obtained from vessels putatively assigned as serving dish. Refitted sherds are known to be the best candidates as they are obviously not residual, however, their low recovery at sites means they are not likely to be regularly available.

The dating of lipid dating pottery the Lower Alsace region provided a further successful test of the CSRA method, on potsherds from a well-dated region. Uncalibrated ^{14}C measurements, statistically identical to the reference measurements on bone collagen and visible residues, were obtained and integrated into the existing seriation and typological study from Lower Alsace. Overall, the radiocarbon dates of pottery vessels from the Alsace region are compatible with the regional seriation and radiocarbon dates on articulated bones supporting the accuracy of the ^{14}C determinations.

These findings mean that dating programs, using compound specific dating of lipid residues, could be used to date the introduction of new commodities, or, more broadly, the introduction and evolution of subsistence practices and animal management (see Chapter 6).

Chapter 6.

CSRA of dairy residues in archaeological pottery vessels

Chapter 6. CSRA of dairy residues in archaeological pottery vessels

6.1 The beginning of dairying

Radiocarbon dating is a useful tool which can be used to date specific archaeological contexts and thus answer various questions regarding, for example, settlement chronologies, specific events or particular objects. The CSRA technique developed in the previous chapters can therefore be applied to specific archaeological questions, especially those related to the use of specific food commodities, such as the timing of the emergence of dairying. Milk consumption in modern populations requires the ability to digest lactose which is lost following weaning, causing symptoms such as stomach cramps, gastric distress, bloating, flatulence and diarrhoea, unless people are 'lactase persistent' (LP) i.e. able to produce an enzyme which aids the transformation of milk sugars, especially lactose, into digestible products (McCracken 1971b). It is generally believed that the evolution of LP was driven by pastoral societies consuming milk products, possibly dating as far back as the Neolithic (*co-evolution* model; McCracken 1971a; Holden and Mace 2009). Another theory is that only populations with LP consumed dairy products (*reverse-cause*; McCracken 1971a). The direct dating of milk residues in potsherds together with the genetic data could, therefore, provide insights into the timing and relationship between the genome evolution and the practice of dairying in Europe.

6.1.1 Milk and lactase persistence in Europe

The ability for adults to digest milk is widespread in Northern and Western Europe, some African countries and in Eastern Asia, but not worldwide (Figure 6-1; Swallow 2003; Itan *et al.* 2010). Interestingly, the digestion of milk is related to different gene variants within

continents, while in Europe it is related to the -13,910*T (Enattah *et al.* 2002; Poulter *et al.* 2003) which increased in frequency between 2,188-20,650 or 7,500-45,000 years ago (Bersaglieri *et al.* 2004; Coelho *et al.* 2005) whereas, in Africa, LP is related to several gene variants, -13,907*G, -13,915*G and -14,010*C with the most recent age estimate of appearance between 2,700 to 6,800 years ago (Ingram and Swallow 2009; Tishkoff *et al.* 2006), suggesting an independent evolution and adaptation to dairy practices through genetic mutations in different places (Tishkoff *et al.* 2006).

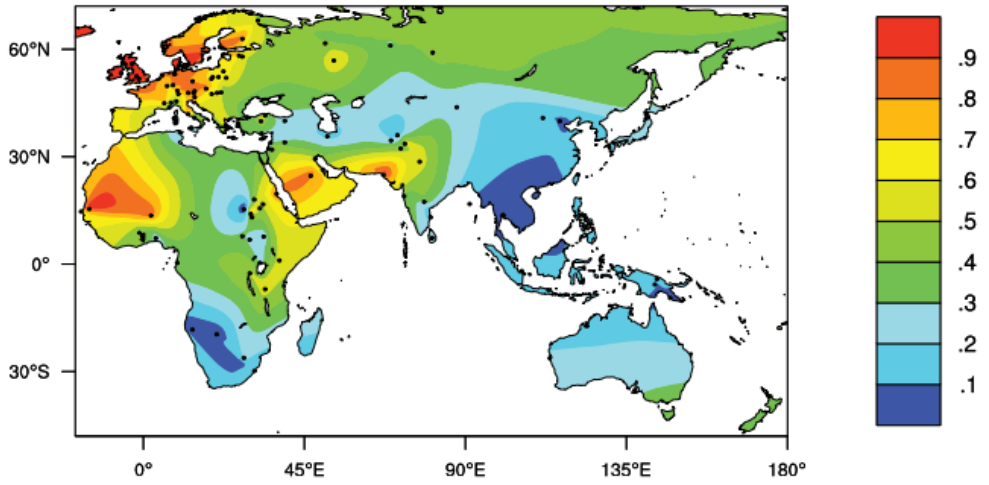

Figure 6-1: Interpolated map of Old World LP phenotype frequencies. Dots correspond to the data locations and colours the frequency of the LP phenotype. From Itan *et al.* (2010, Figure 1).

The study performed by Itan *et al.* (2009) modelled the spatial evolution of the LP-associated (13.910*T) gene variant in Europe based on the hypothesis of a co-evolutionary model for dairying and LP. The model assumes that the evolution and selection of gene were closely related to the LBK culture and increased in frequency 7,500 years ago. However, the theory that the origin of LP is related to dairying practised by the LBK culture was not confirmed by human ancient DNA (aDNA), which failed to discover the LP-associated allele in LBK populations (Burger *et al.* 2007; Witas *et al.* 2015). It should be noted that if the selection of the LP-associated allele did begin during the LBK the frequency at this period may be too low to be discovered in a small number of individuals. Another study from Witas *et al.* (2015),

based on the frequency of LP from a Neolithic Iberian population 5,000 years BC, hypothesised that the diffusion of LP through Europe started in Iberia and reached Northern Europe later and did not follow the route of agriculture and the Neolithisation process (Figure 6-2). However, this hypothesis requires further aDNA studies to be validated.

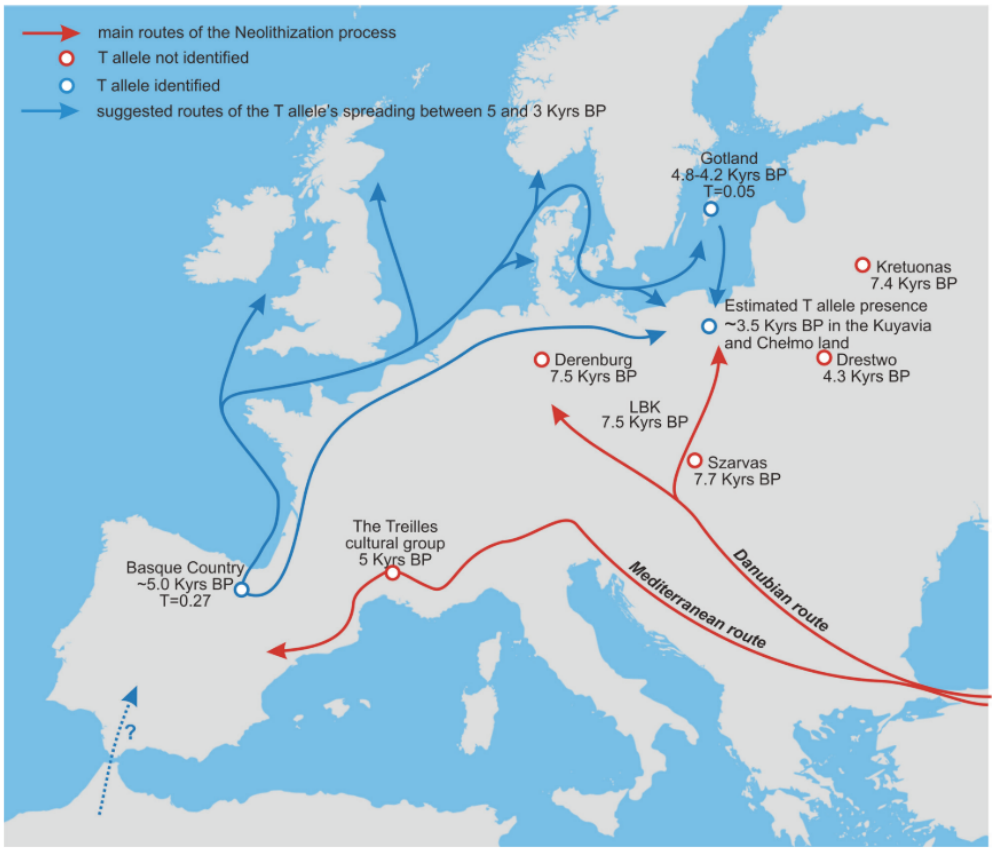

Figure 6-2: Hypothesis on the origin and dispersion of LP-associated gene variant in Europe, based on aDNA studies for the -13.910*T allele, from Witas *et al.* (2015, Figure 5).

6.1.2 Evidence for dairying in archaeological contexts

Clearly, the identification of the beginning of the exploitation of domesticated animals for their secondary products (i.e. obtained during the life of animals, such as milk, wool or blood) as opposed to primary products (i.e. products obtained by the death of the animal such as meat, skin, teeth or horn) is extremely important to determine when and how dairying began. According to Sherratt (1981, 1983) the "secondary product revolution", which was widespread

during the 4th millennium BC in Near East and 3rd millennium BC in Europe, contributed to the intensification of agriculture. His position with regards to the use of milk was criticised and revaluated due to evidence suggesting earlier dairying management at the beginning of the Neolithic (e.g. Vigne and Helmer 2007; Salque *et al.* 2013). Various forms of evidence which could support dairying at sites are iconographic evidences (e.g. Mesopotamian cylinder seals ca. 3500-2900 BC from the Uruk and Jamdat Nasr period (Figure 6-3; Hamilton 1967; Simoons 1971), the mortality profiles produced from faunal assemblages (Payne 1973; Vigne and Helmer 2007), pottery whose form might suggest the processing of milk (Bogucki 1984) and lactase tolerance in populations (e.g. Witas *et al.* 2015).

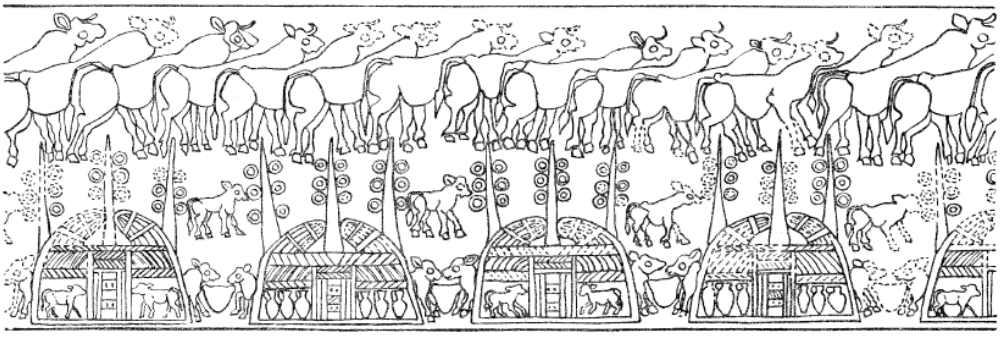

Figure 6-3: Motif of Uruk period cylinder seal showing animal emerging from a hut. From Hamilton (1967, Figure 1).

6.1.2.1 Archaeozoological studies

One of the main sources of evidence for dairying and animal management practices derives from faunal assemblages. Archaeozoological evidence of dairying is first observed by the presence of domesticated animals remains at sites, especially cattle, sheep and goat, which might potentially be exploited for milk production. this can be confirmed by the establishment of mortality profiles (Figure 6-4a) that differ according to the products targeted from the herd, e.g. milk or meat (Payne 1973; Vigne and Helmer 2007). A reference study performed on sheep (Payne 1973) showed that, for meat exploitation, young adults are slaughtered on a large scale,

whereas for dairying purposes lambs less than two months old are killed as sheep can still release their milk even after the death of the lamb. The establishment of mortality profiles for cattle is more difficult due to the lack of modern references and the fact that cows need their calf to release their milk. Therefore, no slaughtering peak of young is expected unless methods to substitute the presence of the calf are employed for the cow to release their milk (Vigne and Helmer 2007).

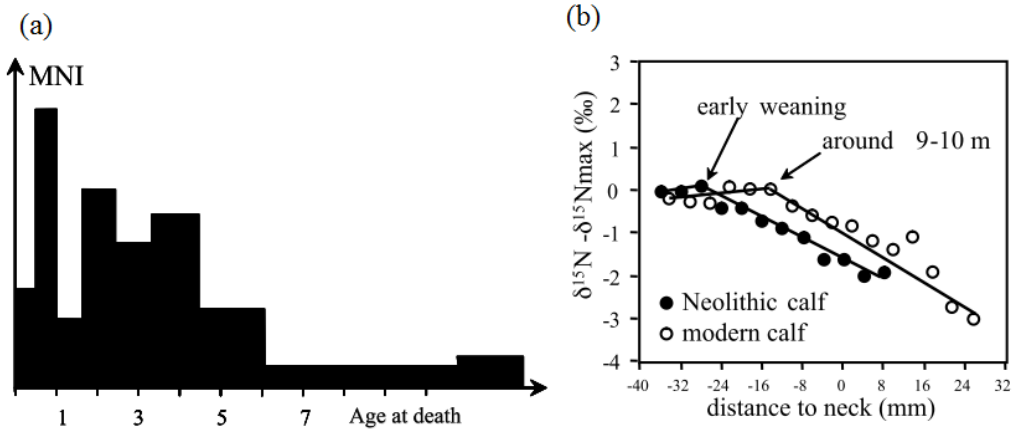

Figure 6-4: Evidence of milk exploitation by (a) cattle mortality profile with a post lactation slaughtering and (b) weaning profiles of a Neolithic calf and modern calf weaned naturally (from Vigne and Helmer 2007, Figure 1).

Such studies can be complemented by the determination of the age of animals at weaning, using $\delta^{15}N$ isotopic analysis from the dentine. Definitive teeth have more depleted $\delta^{15}N$ values than the milk teeth due to the change of diet from high trophic level (milk) to a lower one (grass) and indicate potentially an early weaning of animals which could be related to the exploitation of milk (Figure 6-4b; Balasse *et al.* 1997; Balasse and Tresset 2002).

Vigne and Helmer (2007) summarised the study of 36 caprines and 17 cattle mortality profiles suggesting the exploitation of sheep, goat and cattle for milk during Neolithic as early as the 7th millennium BC in the Balkans and Near East and 6th millennium BC in Mediterranean Europe. More recently Gillis *et al.* (2017) reconstructed cattle mortality profiles across the

LBK culture in Europe during the 6th/5th millennium BC which suggested the exploitation of cattle for both meat and milk products.

6.1.2.2 Evidence of dairying by lipid residue analysis

Direct evidence for secondary product exploitation can be obtained by ORA (Section 1.1.2) of pottery vessels which have shown the processing of dairy products in various region worldwide. To date, the earliest dairy processing during the Neolithic was found in Anatolia with the study of potsherds dated to the 7th millennium BC (Evershed *et al.* 2008b). Following this, during the 6th millennium BC, pottery vessels from several regions in Eastern Europe, Danube, Hungary, Balkans, southern France and Italy revealed evidence for dairy product processing (Craig *et al.* 2005; Salque *et al.* 2012; Debono Spiteri *et al.* 2016; Ethier *et al.* 2017). Dairying started in Saharan Africa (Libya and Algeria) during the Middle Pastoral period in the 5th millennium BC (Dunne *et al.* 2012, 2017; Kherbouche *et al.* 2016). Intensive dairying is seen from the beginning of the Neolithic in Britain and Ireland during the 4th millennium BC (Copley *et al.* 2003, 2005a; Cramp *et al.* 2014b; Smyth and Evershed 2016). Finally, dairy was part of the economy of farming communities in Baltic region during 4th to 2nd millennium BC (Cramp *et al.* 2014a; Pääkkönen *et al.* 2018).

Furthermore, specialist pottery thought to be related to early milk exploitation has been identified by ORA. Sieves with a similar typology to modern 'cheese-strainers' associated with the LBK culture contained dairy products (Figure 6-5; Bogucki 1984; Salque *et al.* 2013; Roffet-Salque and Evershed 2015). Therefore, based on the typology of the pottery and organic residue evidence, the earliest processing of milk into cheese was discovered during the 6th millennium BC in Poland. In contrast, ORA of the so-called 'milk jugs' from middle Copper Age in Hungarian failed to identify dairy residues (Craig *et al.* 2003).

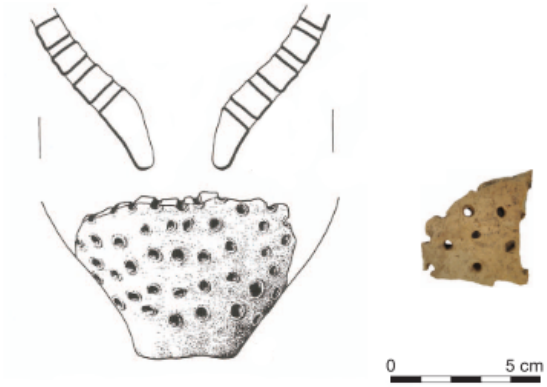

Figure 6-5: Drawing and fragment of a sieve from the Kuyavia region from which dairy residues were detected. From Salque *et al.* (2003, Figure 1).

Recently, studies combine both data from ORA and herd management. Debono Spiteri *et al.* (2016) examined faunal assemblages combined with organic residue analysis of pottery from Neolithic sites along the Mediterranean during 7th to 5th millennium. A total of 82 sites were analysed showing a non-uniformity of dairying practices in the region. Whereas dairy practices were absent around the Aegean Sea and unevenly distributed in the Levant and Anatolia, they were widespread and intense in the Adriatic region and in rock shelters and caves sites in southern France and Iberia. The gradual adoption of dairy products from a meat-based economy, at Gueldaman Cave (Algeria) during the 5th millennium BC, was also supported by combined faunal and ORA studies (Kherbouche *et al.* 2016).

6.1.3 Dating the emergence of dairying

To date, combined ORA and faunal studies have provided valuable knowledge in detecting early dairying practices at archaeological sites, however, the CSRA dating of lipids from these pottery lipid profiles would mark an enormous step in obtaining precise dates for the timing and inception of dairying across Europe.

Based on the hypothesis that dairying in Europe started with the early farmers of central Europe, i.e. the LBK culture, the NeoMilk project (ERC funded) aimed to investigate the

emergence of dairying through a multiscalar approach using: (i) lipid residues in pottery vessels, (ii) butchery practices and mortality profiles of herds, and (iii) archaeological records. The project sampled LBK sites across continental Europe with the combination of methods providing insights into LBK culture and economy and any regional differences. Sites with the best pottery and faunal assemblages from the Hungary, Slovakia, Ukraine, Poland, the Czech Republic, Austria, Germany, France, and the Netherlands, were selected. Spatial and temporal (among LBK phases) lipid residue analysis on pottery from LBK groups were conducted during the project. This allowed insights to be gained into the timing of the emergence of dairying and whether it correlates with the LP diffusion modelled by Itan *et al.* (2009).

At present radiocarbon dating of the LBK is performed by conventional materials such as articulated bones (e.g. Jakucs *et al.* 2016; Denaire *et al.* 2017). Dating of dairy residues from the earliest phases at sites would provide calendar ages for the timing and location of dairying across the LBK area directly on the commodity instead of associated materials or pottery seriation. Especially, it exists sites that cannot be dated by conventional materials due to their poor preservation (e.g. Sierentz, Chapter 5). This approach would allow dating start of dairying in Europe by lipid residues which are very close to the event by archaeological association. Such dating would be highly significant as it would provide chronologies of where and when dairying appeared and also would help determine any time lag between the appearance of the first dairying residues and the evolution of the LP gene. It would also be useful to date dairy residues at sites where small numbers of sherds showed dairy residues, which could correspond either to an early, low frequency of dairying, or, possibly relate to intrusive material, which might bias the picture of the development of dairying at a site. Thus, this would serve as a quality control of the data obtained by ORA. CSRA provides a unique opportunity to work both on the validity of the ORA analysis and temporal spread of dairying by dating directly the commodity and not the associated material(s) from the same contexts.

6.2 Aims and objectives

As noted, this chapter discusses the dating of previously unknown age pottery vessels to provide an example of the use of the CSRA technique to date dairying practices and show the benefits of the technique of CSRA of lipids preserved in pottery vessels to answer archaeological questions.

Firstly, dairy residues from modern (ethnographic; Grillo 2012, 2014) pottery from a selection of settlement and rockshelter sites used by Samburu people from Kenya with extensive knowledge of the use of clay pottery (in everyday consumption and during exceptional times) were dated to provide an example of the value CSRA dating residues for quality control in ORA. The chapter then focusses on the sampling and the dating of residues from the earliest phase at sites from the *Linearbandkeramik* culture which comprised a dairy signature. This will provide insight into the emergence of dairying, by providing direct calendar ages associated to the spatial repartition of dairy during the 5th Millennium BC.

6.3 Dating dairying at an ethnographical site

NB: The dates on potsherds from Samburu are published in Journal of Archaeological Methods and Theory, (Dunne et al. 2018).

6.3.1 Ethnographic sherds from Samburu, Kenya

An ethnographic study performed in 2009 on Samburu pastoralists living in Kenya investigated the relationship between production, use and disposal of clay pottery with subsistence, mobility and ideology (Grillo 2012, 2014). The study describes both the daily and ceremonial use of pottery and also its use in periods of drought and starvation (Grillo 2014). The study showed

that pottery vessels were never used to collect or store milk. This is related to cultural prohibitions which associate milk with the life of the animal and the clay pottery to the death of the animal (as meat is cooked in the pots). The pastoralists consume preferably milk, stored in calabashes, allowing them to keep the herd alive, only consuming meat at feasts and ceremonies, or during periods of drought and only processing it in the clay pottery.

Pottery was sampled from surface contexts from several open-air sites previously occupied by the pastoralist groups and also rockshelters reportedly used for 'meat-feasting'. The ORA results confirmed the processing of mainly ruminant adipose products, with one notable exception, the site of "Naiborkeju" which showed evidence for the processing of dairy products in several potsherds (site map and ORA in Appendix 8.1; Dunne *et al.* 2018). Such results were surprising considering the strong cultural prohibition towards processing milk in clay pots. Several hypotheses could be raised to explain such results, however, the lack of 'memory' of the settlement by the elders from the pastoralists groups suggested an older age for the site. As the potsherds were collected from surface contexts there was no possibility of obtaining a radiocarbon dates for the site aside from the lipids preserved in the pottery, emphasising the importance of being able to reliably date absorbed food residues from pottery vessels, especially when they are the only artefact recovered.

6.3.2 Radiocarbon dates at Samburu

As noted, the presence of dairy products in the Naiborkeju potsherds was unexpected so in order to address this issue it was decided to CSRA date two Samburu potsherds to determine whether they were of truly of ethnographic origin. One further sherd from the site of Latakweny (SAM10) was also dated, to confirm whether it too was of ethnographic (modern) age. This sherd showed $\delta^{13}C$ values on the $C_{16:0}$ and $C_{18:0}$ FAs characteristic of ruminant adipose fats.

The dates of the $C_{16:0,}$ $C_{18:0}$ and $C_{18:1}$ FAs showed a weighted average on the fraction modern of 1.0762 ± 0.0025 (T'= 1.1, T'(5%) = 6.0, υ = 2) corresponding to a post-bomb peak age calibrated to 2002-2004 AD with a 95 % probability (Table 6-1). This clearly demonstrates clearly the ethnographic origin of the potsherd from the Latakweny settlement.

Table 6-1: CSRA dates on potsherds from Latakweny and Naiborkeju.

Sample	BRAMS #	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	Calibrated age (AD)	σ range
SAM10-$C_{16:0}$	1594.2.1	395	1.0747 ± 0.0034	-579 ± 27	2002-2005 (92.7 %)	
SAM10-$C_{18:0}$	1594.2.2	570	1.0790 ± 0.0034	-611 ± 27	2001-2004 (92.6 %)	•
SAM10-$C_{18:1}$	1594.2.3	350	1.0747 ± 0.0035	-579 ± 27	2002-2005 (92.7 %)	
SAM15/3-$C_{16:0}$	1596.1.1	176	0.9887 ± 0.0035	91 ± 31	1680-1764 (31.5%) 1801-1895	•
SAM15/3-$C_{18:0}$	1596.1.2	156	0.9810 ± 0.0037	154 ± 32	(49.4%) 1902-1939 (14.5%)	
SAM14/6-$C_{16:0}$	1597.1.1	151	0.9767 ± 0.0036	189 ± 31	1664-1764 (17.6%) 1726-1813	•
SAM14/6-$C_{18:0}$	1597.1.2	190	0.9812 ± 0.0036	153 ± 30	(57.2%) 1918-… (20.6%)	

• $C_{16:0}$ and $C_{18:0}$ (and $C_{18:1}$) dates identical within 1σ

The two sherds from the Naiborkeju site, one comprising dairy products (SAM15/3) and the other ruminant adipose products (SAM14/6) were CSRA dated. The measurements on both FAs are statistically identical (T'= 2.5, T'(5%) = 3.8, υ = 1 for both) which supports their contemporaneity. The combined measurements on the FAs, yielded pre-bomb peak uncalibrated ages of 171 ± 22 BP (SAM15/3) and 122 ± 22 BP (SAM14/6). It should be noted that the part of the calibration curve where the data are plotted presents as a plateau and thus the age of the potsherds likely falls within the range of the 17th to 20th centuries (Table 6-1). It is not possible to be more precise, however, the calibration demonstrates that the potsherds were used in the historic period rather than in recent times. This data validates the hypothesis that potsherds recovered from the Naiborkeju area did not originate from modern Samburu pastoralists.

6.3.3 Conclusions

The ^{14}C determinations on the potsherds from the Samburu ethnographic study provides an example of the value of CSRA dating, especially in addressing questions of quality control/authenticity. It is clear that information derived from lipid residue analysis could lead to erroneous conclusions (e.g. that milk was processed in clay vessels despite the known cultural prohibition against this), particularly if potsherds do not come from secure contexts. In this instance, the technique of CSRA was uniquely suited to unravel questions related to the adoption/consumption/storage of specific foodstuffs by dating directly lipid residues from such commodities.

6.4 Dating early dairying in Europe during the LBK

6.4.1 Sites selection for dating dairy residues

6.4.1.1 LBK sites with evidence for dairy residues in pottery vessels

LBK sites analysed during the NeoMilk project (at the time of the analysis) which contained lipid residues, indicative of dairy processing, in pottery vessels are presented in Figure 6-6. Preliminary lipid residue results from the NeoMilk project showed a variable picture during the LBK with regions showing either strong, limited or no evidence for dairy product exploitation. From the data available, dairying was shown to be widely present at LBK sites in the Hungarian region, North East Poland, West to the Upper-Alsace, the Parisian Basin, the Netherlands and North West Germany. In the remainder of Europe, sites from Austria, South Germany, Lower-Alsace, the Czech Republic or Ukraine show no evidence for dairying activities from ORA or show only limited evidence (either 1 or 2 potsherds per site or lipid residues plotting at the edge of ruminant/dairy fats reference ellipses).

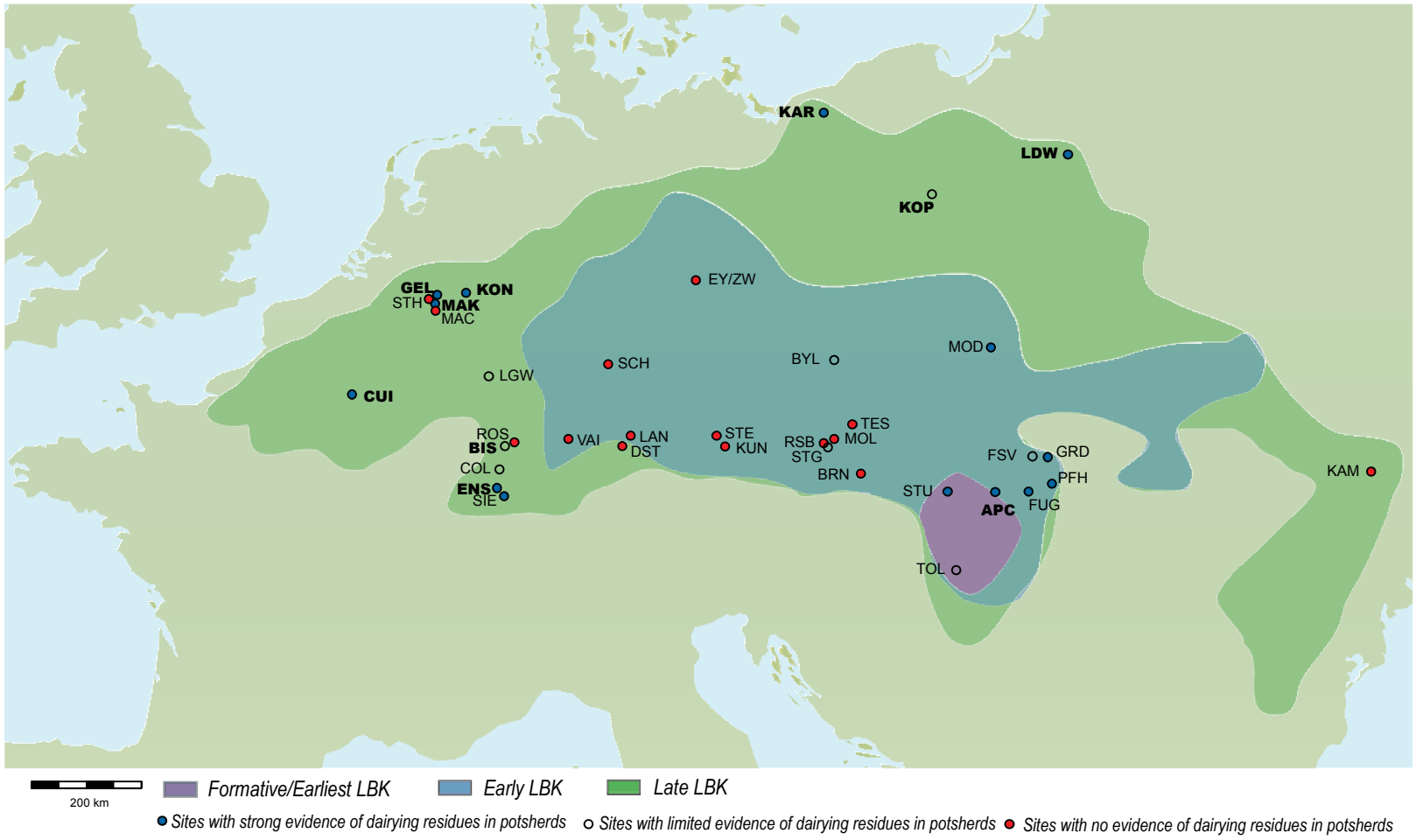

Figure 6-6: Map of LBK sites with evidence of dairying residues in pottery vessels. The sites with limited evidence of milk products corresponds to the ones with only 1 to 3 sherds with dairying residues or at the edge of ruminant adipose/dairy fats. Sites in bold are the ones selected for radiocarbon dating. Sites abbreviations are APC: Apc-Berekalja I, BIS: Bischoffsheim, BYL: Bylany, COL: Colmar, CUI: Cuiry-les-Chaudardes, DST: Dillingen-Steinheim, ENS: Ensisheim, EY/ZW: etyra-Swenkau, FSV: Felsővadász-Várdomb, FUG: Füzesabony-Gubakút, GEL: Geleen-Janskamperveld, GRD: Garadna, KAM: Kamyane-Zavallia, KAR: Karwowo 1, KON: Konigshoven 14, KOP: Kopydłowo, KUN; Künzing-Unternberg, LAN; Langenreichen am Burgholz, LDW: Ludwinowo 7, LGW: Langweiler 8, MAC: Maastricht-Cannerberg, MAK: Maastricht-Klinkers, MOL: Mold, PFH: Polgár-Ferenci-há, ROS: Rosheim, RSB: Rosenburg, SCH: Schwanfeld, SIE: Sierentz, STE: Stephansposching, STG: Stroegen, STH: Stein-Heidekampweg, STU: Štúrovo, TES: Těšetice-Sutny, TOL: Tolna-Mözs and VAI: Vaihingen.

Interestingly, sites at the periphery of the LBK settlement show intensive dairying, whereas the more 'central' sites demonstrate either limited, or, no evidence, for dairying.

6.4.1.2 Sampling strategy

The fatty acid carbon isotope-based interpretations of lipid residues of dairy fats came from the NeoMilk database (with the data available at the time of analysis). The sherds which showed a dairy signal were assumed not to demonstrate any reservoir effect. A sampling strategy was established to date early dairying and the sites selected based on the following criteria:

(i) Presence of dairy residues in pottery vessels;

(ii) The potential to sample sherds from the earliest phase at the site showing dairy residues;

(iii) Presence of sherds with lipid concentrations above 500 $\mu g.g^{-1}$;

(iv) The possibility to pair ^{14}C measurements with at least one other sherd with sufficient lipid concentration (either dairy or adipose) from the same phase/context.

The criteria presented in points (i) and (ii) are necessary to be able to date the earliest dairy residues from sites, for example, if several phases present dairy residues, then the first phase which contains such residues must be sampled. The point (iii) was determined based on the finding discussed in Chapter 4 to ensure that sufficient C would be extracted from the potsherd for a radiocarbon measurement. The last point (iv) is of particular importance as it will allow the detection of outliers/intrusive pottery as most of the LBK pottery are single undecorated sherds. A minimum of two ^{14}C determinations from two different potsherds should be recorded at each site. If only one sherd with dairy residues can be dated, then another sherd with adipose fats should be sampled.

Surprisingly, the preservation of dairy fats in pottery, in terms of concentrations, was poor and almost half the sites discussed (especially the Hungarian ones) comprised dairy residues in concentrations too low to obtain a radiocarbon date. This could suggest either that dairy residues were used in low amount or, have poorer preservation in the potsherds than the carcass fats at these particular sites. Another constraint relates to the size of potsherds which, in certain cases, were too small for a second sampling for dating. A total of 10 sites from Hungary to Poland and the West (France, Netherlands, Germany; Figure 6-6), which matched the criteria detailed above, were sampled to provide a general overview of the spatial distribution of sites where dairying occurred during the LBK.

6.4.2 CSRA determinations

A total of 28 pottery vessels from the 10 LBK sites selected were prepared for ^{14}C dating (Table 6-2; ORA details in Appendix 8.3). It should be noted there are regional differences for the LBK phases, thus, in this chapter, the phases correspond to the chronologies previously established for each site/region, e.g. the phase IIB from Poland, II from Alsace and IIb from the Netherlands do not relate to the same time period due to the regional differences.

The ^{14}C measurements (Table 6-2) successfully passed the internal criteria for the $C_{16:0}$ and $C_{18:0}$ FAs for 15 sherds (identical within a 2-σ error), five failed the internal test, five generated only one target, and three provided insufficient carbon to be dated. Presented below are the results obtained on a site-by-site basis.

Table 6-2: Radiocarbon measurements from LBK sites with dairying residues recovered from the potsherds. The phases correspond those associated with sites the regional chronology.

Sample	BRAMS #	Phase	Context	m CO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range	Comments
APC-C-4217-$C_{16:0}C_{18:0}$	1925.1.1	Earliest	697	56	-	-	-	Dairy fats
APC-C-4200	-		589	-	-	-	-	Dairy fats
BIS-C-4519-$C_{16:0}$	1221.1.1	Late IVa1	538	265	0.4551 ± 0.0018	6,284 ± 32	X	Non-ruminant adipose fats
BIS-C-4519-$C_{16:0}$	1221.1.2	Late IVa1	538	315	0.4655 ± 0.0018	6,102 ± 31		
BIS-C-4527-$C_{16:0}$	1705.1.1	Late IVa1	538	202	0.4689 ± 0.0018	6,084 ± 32	•	Dairy fats
BIS-C-4527-$C_{18:0}$	1705.1.2	Late IVa1	538	301	0.4686 ± 0.0017	6,090 ± 31		
BIS-C-4529-$C_{16:0}$	1209.1.1	Late IVa1	538	285	0.4612 ± 0.0018	6,177 ± 31	••	Ruminant adipose fats
BIS-C-4529-$C_{18:0}$	1209.1.2	Late IVa1	538	386	0.4654 ± 0.0018	6,103 ± 30		
BIS-C-4531-$C_{16:0}$	1267.1.1	Late IVa1	538	108	0.4631 ± 0.0031	6,185 ± 57	••	Non-ruminant adipose fats
BIS-C-4531-$C_{18:0}$	1267.1.2	Late IVa1	538	195	0.4673 ± 0.0024	6,112 ± 44		
ENS-C-5913-$C_{16:0}$	1915.1.1	Early II	9	347	0.4538 ± 0.0017	6,345 ± 31	•	Dairy fats
ENS-C-5913-$C_{18:0}$	1915.1.2	Early II	9	443	0.4563 ± 0.0017	6,303 ± 31		
ENS-C-5915-$C_{16:0}$	1916.1.1	Early II	9	300	0.4518 ± 0.0017	6,383 ± 32	••	Dairy fats
ENS-C-5915-$C_{18:0}$	1916.1.2	Early II	9	275	0.4557 ± 0.0017	6,314 ± 33		
ENS-C-5934-$C_{16:0}$	1958.1.1	Early II	28	291	0.4575 ± 0.0016	6,282 ± 30	•	Dairy fats
ENS-C-5934-$C_{18:0}$	1958.1.2	Early II	28	303	0.4588 ± 0.0016	6,258 ± 30		
ENS-C-5940-$C_{16:0}$	2031.1.1	Early II	28	190	0.4643 ± 0.0018	6,162 ± 33	••	Ruminant adipose fats
ENS-C-5940-$C_{18:0}$	2031.1.2	Early II	28	406	0.4599 ± 0.0016	6,239 ± 30		
CUI-C-5708-$C_{16:0}$	1917.1.1	Late I	25	184	0.4592 ± 0.0018	6,252 ± 34	•	Dairy fats
CUI-C-5708-$C_{18:0}$	1917.1.2	Late I	25	144	0.4611 ± 0.0019	6,218 ± 36		
CUI-C-5776-$C_{16:0}C_{18:0}$	2020.1.1	Late II	378	242	0.4655 ± 0.0018	6,142 ± 32	-	Dairy fats
CUI-C-5801-$C_{16:0}$	2021.1.1	Late II	386	443	0.4658 ± 0.0016	6,138 ± 30	•	Dairy fats
CUI-C-5801-$C_{18:0}$	2021.1.2	Late II	386	388	0.4660 ± 0.0016	6,134 ± 30		
CUI-C-5735-$C_{16:0}$	1918.1.1	Late III	241	141	0.4658 ± 0.0020	6,138 ± 37	-	Dairy fats
CUI-C-5735-$C_{18:0}$	1918.1.2	Late III	241	98	-	-		
KON-C-5594-$C_{16:0}$	2029.1.1	Early	522	638	0.4591 ± 0.0016	6,253 ± 29	••	Ruminant adipose fats
KON-C-5594-$C_{18:0}$	2029.1.2	Early	522	965	0.4566 ± 0.0015	6,298 ± 29		
KON-C-5598-$C_{16:0}$	2026.1.1	Early	522	145	0.4576 ± 0.0019	6,106 ± 34	•	Dairy fats
KON-C-5598-$C_{18:0}$	2026.1.2	Early	522	180	0.4557 ± 0.0018	6,139 ± 34		
KON-C-5617-$C_{16:0}$	2023.1.1	Early	522	117	0.4692 ± 0.0022	6,078 ± 39	X	Dairy fats
KON-C-5617-$C_{18:0}$	2023.1.2	Early	522	361	0.4614 ± 0.0016	6,213 ± 30		
GEL-C-3271-$C_{16:0}$	2027.1.1	I	49015	232	0.4452 ± 0.0017	6,500 ± 33		Dairy fats
GEL-C-3271-$C_{18:0}$	2027.1.2	I	49015	43	-	-	-	
GEL-C-3276-$C_{16:0}C_{18:0}$	1923.1.1	I	49015	232	0.4595 ± 0.0018	6,142 ± 33	-	Dairy fats

Sample	BRAMS #	Phase	Context	m CO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range	Comments
GEL-C-3298-$C_{16:0}$	2032.1.1	II	53010.04	272	0.4628 ± 0.0017	6,188 ± 31	••	Ruminant adipose fats
GEL-C-3298-$C_{18:0}$	2032.1.2	II	53010.04	732	0.4592 ± 0.0016	6,253 ± 29		
GEL-C-3299-$C_{16:0}$	1924.1.1	II	53010.05	275	0.4563 ± 0.0017	6,304 ± 32	X	Dairy fats
GEL-C-3299-$C_{18:0}$	1924.1.2	II	53010.05	932	0.4483 ± 0.0016	6,444 ± 30		
MAK-C-3094-$C_{16:0}$	2022.1.1	IIb	207	302	0.4736 ± 0.0017	6,002 ± 30	X	Non-ruminant adipose fats
MAK-C-3094-$C_{18:0}$	2022.1.2	IIb	207	947	0.4593 ± 0.0016	6,251 ± 29		
MAK-C-3099-$C_{16:0}C_{18:0}$	1922.1.1	IIb	207	-	0.4465 ± 0.0020	6,300 ± 37	-	Dairy fats
KAR-C-3636-$C_{16:0}$	2028.1.1		47	430	0.4636 ± 0.0016	6,176 ± 30	••	Non-ruminant adipose fats
KAR-C-3636-$C_{18:0}$	2028.1.2		47	413	0.4604 ± 0.0016	6,230 ± 30		
KAR-C-3677-$C_{16:0}$	2025.1.1		43	385	0.4590 ± 0.0016	6,255 ± 30	•	Dairy fats
KAR-C-3677-$C_{18:0}$	2025.1.2		43	235	0.4614 ± 0.0017	6,214 ± 32		
KOP-C-2949-$C_{16:0}$	1920.1.1		25 B	65	-	-	-	Dairy fats
LDW-C-2267-$C_{16:0}$	2024.1.1	IIB	A49	159	0.4637 ± 0.0019	6,173 ± 36	•	Non-ruminant adipose fats
LDW-C-2267-$C_{18:0}$	2024.1.2	IIB	A49	419	0.4634 ± 0.0016	6,179 ± 30		
LDW-C-2272-$C_{16:0}$	1919.1.1	IIB	A50	225	0.4650 ± 0.0018	6,150 ± 33	X	Dairy fats
LDW-C-2272-$C_{18:0}$	1919.1.2	IIB	A50	315	0.4574 ± 0.0017	6,283 ± 32		

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ
X $c_{16:0}$ and $C_{18:0}$ dates non-identical within 2σ

6.4.2.1 APC -Berekalja I (APC)

Two sherds with lipid residues denoting dairy processing were selected, unfortunately, not enough C for a ^{14}C measurement could be extracted, thus preventing the dating of this Hungarian site by CSRA.

One measurement on bone collagen, from the same context (pit 697) as one of the sherds selected, dated to 6,290 ± 40 BP (OxA-25187; Jakucs *et al.* 2016). This corresponds to the earliest LBK phase at the site and thus gives an indirect contemporaneous date on dairying practices, calibrated to 5,309 – 5,226 cal BC (68 % probability) or 5,366 – 5,207 cal BC (95 % probability).

6.4.2.2 Bischoffsheim (BIS)

The dating of sherds from the site of Bischoffsheim was presented in Chapter 5. In the current chapter, one further sherd with a dairy residue from the LBK IVa1 was selected for ^{14}C dating (Table 6-2).

The measurements on the sherd with a dairy residue was combined to give a date of 6,087 ± 26 BP (BIS-C-4527; T' = 0.2, T'(5 %) = 3.8, υ = 1). A total of three sherds with ruminant adipose from the same phase and pits were also dated in Chapter 5, of these, BIS-C-4519 failed the internal criteria but the other two provided results which were identical within a 2σ error. Their weighted average (excluding BIS-C-4519-$C_{16:0}$) is of 6,132 ± 16 BP (T' = 5.0, T'(5 %) = 9.5, υ = 4). Uncalibrated measurements on the dairy residue are statistically identical to those of adipose fats (T' = 7.5, T'(5 %) = 12.6, υ = 6). The date on the dairy fat is thus in agreement with LBK IVa1 on a simple statistical basis, however, when calibrated, the

sherd BIS-C-4527 is dated to 5,198 – 5,158 cal BC (3 % probability) or 5,066 - 4,939 cal BC (93 % probability; Figure 6-7).

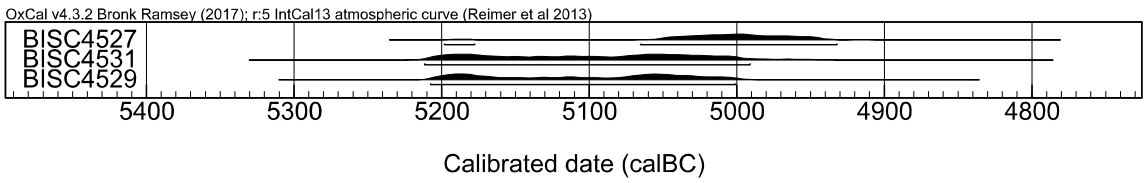

Figure 6-7: Probability distribution of radiocarbon dates for dated potsherds at the site of Bishoffsheim (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

The Bayesian statistical model of the LBK in Lower Alsace presented by Denaire *et al.* (2017, Figure 8) included 56 radiocarbon dates, 10 of which are from the LBK phase IVa1, and estimated the start of LBK IVa1 at 5,210 - 5,145 cal BC with an end date of 5,185 – 5,110 cal BC (95 % probability). If the measurement on the potsherd BIS-C-4527 is accurate it should fit in the original model, however, only the lowest calibration estimates to 5,198 – 5,158 cal BC, with a 3% probability, fit the reference range and it would be likely that if included in the statistical model this potsherd would be rejected.

Supporting this hypothesis, one pig collagen sample (close in age to potsherd BIS-C-4527) from the phase IVb at BIS which was dated to 6084 ± 34 BP (SUERC-46509) had a poor agreement in the original model (A: 29) and was interpreted as being too young for the LBK (Denaire *et al.* 2017). Therefore, the sherd BIS-C-4527 which exhibits a similar ^{14}C measurement is also likely too young for the LBK in the region (which ended 5,185 – 5,110 cal BC (95 % probability)) and could be an intrusive sherd. Such an explanation could explain the low abundance of dairy residues during the LBK at BIS during the phase IVa1 (see Chapter 5).

6.4.2.3 Ensisheim (ENS)

Pottery from the early phase II at the site of Ensisheim was sampled and four sherds, three dairy residues and one ruminant adipose fat, yielded enough lipid for ^{14}C measurement. Based on the FAs dates the two potsherds from pit 9 are dated to 6,324 ± 26 BP (ENS-C-5913; T' = 0.9, T'(5%) = 3.8, υ = 1; dairy residue) and 6,348 ± 26 BP (ENS-C-5915; T' = 2.3, T'(5%) = 3.8, υ = 1; dairy residue). These two potsherds thus showed statistically identical dates on two dairy residues (T' = 0.6, T'(5%) = 3.8, υ = 1) which are calibrated to 5,361 – 5,224 cal BC for ENS-C-5913 and 5,461 – 5,230 cal BC for ENS-C-5915 (95 % probability for both; Figure 6-8).

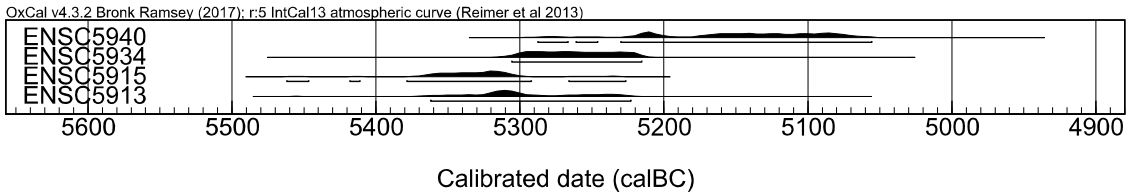

Figure 6-8: Probability distribution of radiocarbon dates for potsherds from the site of Ensisheim (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

The FAs from the potsherds from pit 28 are dated to 6,270 ± 25 BP (ENS-C-5934; T' = 0.3, T'(5%) = 3.8, υ = 1; dairy residue) and 6,206 ± 26 BP (ENS-C-5940; T' = 3.0, T'(5%) = 3.8, υ = 1; adipose residue). They exhibit younger dates than those of pit 9 and are not statistically consistent (T' = 4.3, T'(5%) = 3.8, υ = 1). Pot ENS-C-5934 (dairy residue) is calibrated to 5,306 – 5,216 cal BC (95 % probability) and pot ENS-C-5940 (adipose residue) is calibrated to 5,284 – 5,056 cal BC (95 % probability; Figure 6-8). It appears that, in contrast to pit 9, pit 28 yielded pottery originating from the LBK phase III associated with potsherds from the phase II and thus, could corresponds to a pit representing the transition from the early/middle LBK at the site (Jeunesse and Sainty 1992). The inconsistency of dates obtained from pottery from

pit 28 could therefore, reflect the use of the pit for several generations or suggest that one of the potsherds is residual/intrusive.

6.4.2.4 Cuiry-les-Chaudardes (CUI)

A total of four sherds with dairy residues from the late LBK phases I, II and III at the site were selected. The measurements on the combined FAs from potsherd extract from the phase I gave a date of 6,236 ± 27 BP (CUI-C-5708; T' = 0.5, T'(5 %) = 3.8, υ = 1) and calibrated to 5,296 – 5,209 cal BC (68 % probability) or 5,303 – 5,076 cal BC (95 % probability; Figure 6-9).

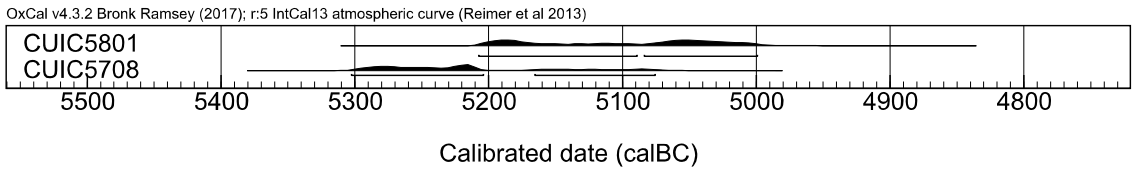

Figure 6-9: Probability distributions of radiocarbon dates for potsherds from the site of Cuiry-les Chaudardes (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

The FAs of two sherds Phase II were dated, one yielded a date of 6,136 ± 25 BP (CUI-C-5801; T' = 0.0, T'(5 %) = 3.8, υ = 1) and the other where the two FAs were combined as one target was dated to 6,142 ± 32 BP (CUI-C-5776). The potsherd CUI-C-5801, which passed the internal quality control was calibrated to 5,203 – 5,026 cal BC or 5,208- 5,002 cal BC (68 and 95 % probability, respectively; Figure 6-9). The phase III was dated to 6,138 ± 37 BP (CUI-C-5735) by one target only. The calibrated potsherd dates from the phases I and II agree with the succession of LBK phases I and II at the site and, thus, supports the relative chronology of the two potsherds.

Dates from bones are available for this site (Constantin and Blanchet 1998; Dubouloz 2003). However, the measurements were performed by thermoluminescence dating with uncertainties of around 150 years, making a rigorous comparison with these to the lipid dates difficult.

6.4.2.5 Konigshoven 14 (KON)

Two potsherds with FAs assigned to dairy fat and one to ruminant adipose fats, from the early LBK phase (pit 522) of the site at Konigshoven, were submitted to ^{14}C measurement. One vessel which contained dairy products failed the internal quality control (KON-C-5617; T' = 7.5, T'(5%) = 3.8, υ = 1). Identical dates of 6,276 ± 24 BP (KON-C-5594; T' = 1.2, T'(5%) = 3.8, υ = 1; adipose residue), and 6,123 ± 27 BP (KON-C-5598; T' = 0.5, T'(5%) = 3.8, υ = 1; dairy residue), were successfully obtained from the other two pots.

When calibrated, the dates from potsherd KON-C-5594 (comprising ruminant adipose residues) ranged from 5,300 – 5,228 cal BC (68 % probability) or 5,308 – 5,217 cal BC (95 % probability; Figure 6-10). Despite the fact that the potsherds originated from the same context, the dairy residue from pot KON-C-5598 produced younger dates, calibrated to 5,198 – 5,000 cal BC (68 % probability) or 5,208 – 4,986 cal BC (95 % probability). This might suggest the use of this pit for several generations or, possibly, mean that one of the sherds is residual/intrusive.

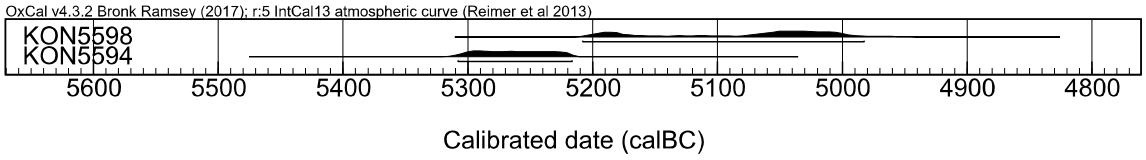

Figure 6-10: Probability distributions of radiocarbon dates for potsherds from the site of Konigshoven (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

6.4.2.6 Geleen-Janskamperve (GEL)

Two potsherds (comprising dairy residues) from phase Ib and two potsherds from phase II (one dairy, one ruminant adipose products) from the site of Geleen-Janskamperve were CSRA dated. The results showed significant variability.

First, for the phase Ib the only date on the pot GEL-C-3271 was 6,500 ± 31 BP, which appears to be too old for a known LBK settlement. The other potsherd from the same context was dated by one target to 6,142 ± 33 BP (GEL-C-3276), which is significantly younger.

For phase II, one pot measurement was combined to 6,224 ± 25 BP (GEL-C-3298; T' = 2.3, T'(5%) = 3.8, υ = 1; adipose residue), whereas, the second sherd failed the internal quality control (GEL-C-3299; T' = 10.2, T'(5%) = 3.8, υ = 1; dairy residue). The ^{14}C measurement of potsherd GEL-C-3298 which passed the internal quality control was calibrated to 5,290 – 5,079 cal BC (68 % probability) and 5,298 – 5,070 cal BC (95 % probability; Figure 6-11). This provide an indirect date on adipose residue from the same context than the dairy residue.

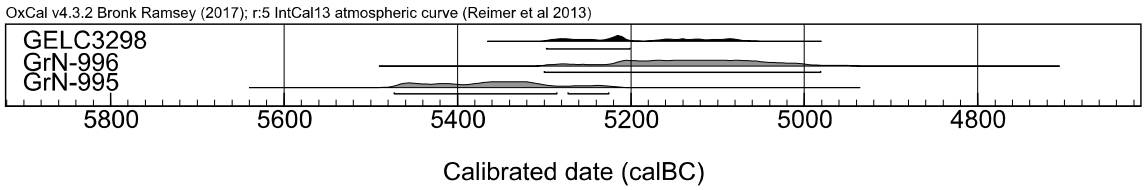

Figure 6-11: Probability distributions of radiocarbon dates for potsherds from the site of Geleen-Janskamperve. Dates in black correspond to the pot which passed the internal control and in grey the dates on charcoals (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

Two ^{14}C measurements on charcoal were previously recorded at the site for phase Ib (but other contexts). These dated to 6,370 ± 60 BP (GrN-995) and to 6,175 ± 60 BP (GrN-996), again showing significant variability within the same phase (Lanting and van der Plicht 2015). It is possible that these charcoals are affected by an old wood effect, especially date GrN-995. The other date GrN-996 is identical within a 2-σ error to the single FA measurement on dairy residues of the same phase from potsherd GEL-C-3276 (T' = 0.2, T'(5%) = 3.8, υ = 1). When calibrated the charcoal date (GrN-996) ranges from 5,214 – 5,050 cal BC (68 % probability) or 5,300 – 4,982 cal BC (95 % probability; Figure 6-11).

6.4.2.7 Maastricht-Klinkers (MAK)

The FAs of two pottery vessels comprising dairy and non-ruminant adipose fats were dated. The dating of the dairying residue failed the internal control, with the date on the $C_{16:0}$ clearly showing modern contamination (T' = 39.1, T'(5%) = 3.8, υ = 1). The date of the $C_{18:0}$ fatty acid (6,251 ± 29 BP, BRAMS-2022.1.2) is identical within a 2-σ range to the combined $C_{16:0}$ and $C_{18:0}$ date on the second pot (6,300 ± 37 BP, MAK-C-3099; T' = 1.1, T'(5%) = 3.8, υ = 1; adipose residue), suggesting good agreement between the two vessels. However, those measurement do not present an internal control.

6.4.2.8 Karwowo 1 (KAR)

Two sherds from the site of Karwowo comprising dairy and non-ruminant adipose fats based on their FA carbon isotope values, were dated. Both passed internal quality control and gave combined dates to 6,204 ± 25 BP (KAR-C-3636; T' = 1.6, T'(5%) = 3.8, υ = 1; adipose residue) and to 6,236 ± 26 BP (KAR-C-3677; T' = 0.9, T'(5%) = 3.8, υ = 1; dairy residue), which are statistically identical (T' = 0.8, T'(5%) = 3.8, υ = 1). Potsherd KAR-C-3636 is calibrated to 5,217 – 5,205 or 5,286 – 5,054 cal BC (68 and 95 % probability, respectively) and KAR-C-3677 is calibrated to 5,296 – 5,209 or 5,303 – 5,076 cal BC (68 and 95 % probability respectively; Figure 6-12).

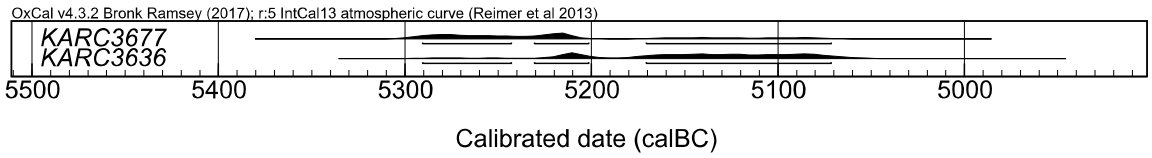

Figure 6-12: Probability distribution of radiocarbon dates for potsherds from the site of Karwowo (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

6.4.2.9 Kopydłowo (KOP)

The potsherd selected from the site of Kopydłowo (KOP-C-2949) corresponded to the only one with dairy residues at the site (excepting sieves) and could either correspond to an intrusive sample or a specialised vessel for dairy product processing, considering its small size compared to the other vessels submitted to ORA (Roffet-Salque and Evershed 2015). Unfortunately, insufficient C was extracted to allow a ^{14}C measurement.

6.4.2.10 Ludwinowo 7 (LDW)

At the site of Ludwinowo two pots, one comprising a dairy residue and the other ruminant adipose fat, from the phase IIB, were dated. While the date from the sherd with adipose residue is combined to 6,177 ± 26 BP (LDW-C-2267; T' = 0.0, T'(5 %) = 3.8, υ = 1), the date on the sherd containing dairy products failed the internal quality control (LDW-C-2272; T' = 8.4, T'(5 %) = 3.8, υ = 1). The potsherd LDW-C-2272 yielded a calibrated date of 5,207 – 5,072 cal BC (68 %) or 5,216 – 5,048 cal BC (95 % probability; Figure 6-13).

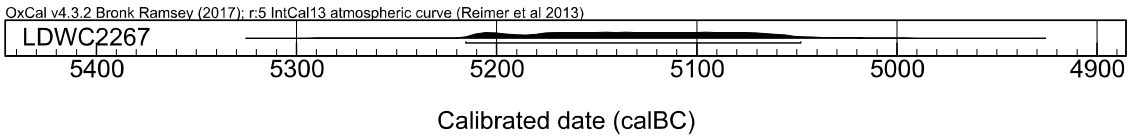

Figure 6-13: Probability distribution of radiocarbon dates for potsherds from the site of Ludwinowo 7 (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

6.4.3 Mapping dairying in the Neolithic Europe

6.4.3.1 Chronology of early dairying

A total of eight sites were dated using sherds which contained dairy or adipose fat residues. The majority of the pottery passed the internal quality control criterion, but five potsherds failed

and three had no internal control, suggesting that those are not reliable and were thus disregarded. In summary, none of the potsherds from Maastricht-Klinkers (Netherlands) site gave reliable results based on the internal quality control criterion. At the sites of Ludwinowo (Poland) and Geleen-Janskamperveld (Netherlands), only the potsherds comprising adipose residues passed the internal quality control thus it provides an indirect radiocarbon date for the same phase/context of the earliest dairy residues at the sites. In addition, at the site of Bischoffsheim (France), the date on the sherd containing dairy products possibly suggests an intrusive sherd, thus this site is not included in the discussion. Nonetheless, for the other sites, there is an overall good agreement between the dates on dairy and adipose fat residues from the same phases, denoting their contemporaneity.

All the dates (dairy and adipose fats) from Cuiry-les-Chaudardes, Ensisheim (France), Geleen-Janskamperveld, Maastricht-Klinkers, (the Netherlands), Konigshoven (Germany), Karwowo and Ludwinowo (Poland) were compared in a simple model to estimate the beginning of dairying (Figure 6-14). The model shows overall good agreement (A_{model}: 85) with all measurements on the potsherds agreeing, with one exception (ENS-C-5915, A: 59). The commencement of dairy exploitation was estimated to 5,347 – 5,303 (39 %) or 5,282 - 5,238 cal BC (29 % probability) or 5,383 – 5,230 cal BC (95% probability). Its posterior distribution with 68 % probability presents a bimodality for the two dates on potsherds containing dairy residues at Ensisheim, due to them both hitting two wiggles on the calibration curve.

The oldest dates obtained from dairy lipid residues were obtained at Ensisheim, France and dated to 5,354 – 5,220 cal BC (95 % probability), followed by Cuiry-les-Chaudardes, France 5,303 – 5,118 cal BC (95 % probability) for the late phase I and 5,214 - 5,051 cal BC (95 %) for phase II. Following these earliest dates, North Germany (Konigshoven) was dated to

5,213 – 5,042 directly on dairy residues or to 5,302 – 5,216 cal BC (95 % probability) on adipose products which showed similar age range as Geleen-Janskamperveld, Netherlands, where the earliest dairy context is dated to 5,298 – 5,084 cal BC (95 % probability) from adipose fats. The Polish sites showed dairy residue results from the site of Karwowo dated to 5,303– 5,119 cal BC (95 % probability) as opposed to Ludwinowo which showed later dates on adipose residues to 5,221 – 5,079 (95 % probability). These results suggest different times of inception for the adoption of dairying practices across the LBK settlements in central Europe between the 53rd and 52nd century BC, although the timescale is relatively short at only one or two generations.

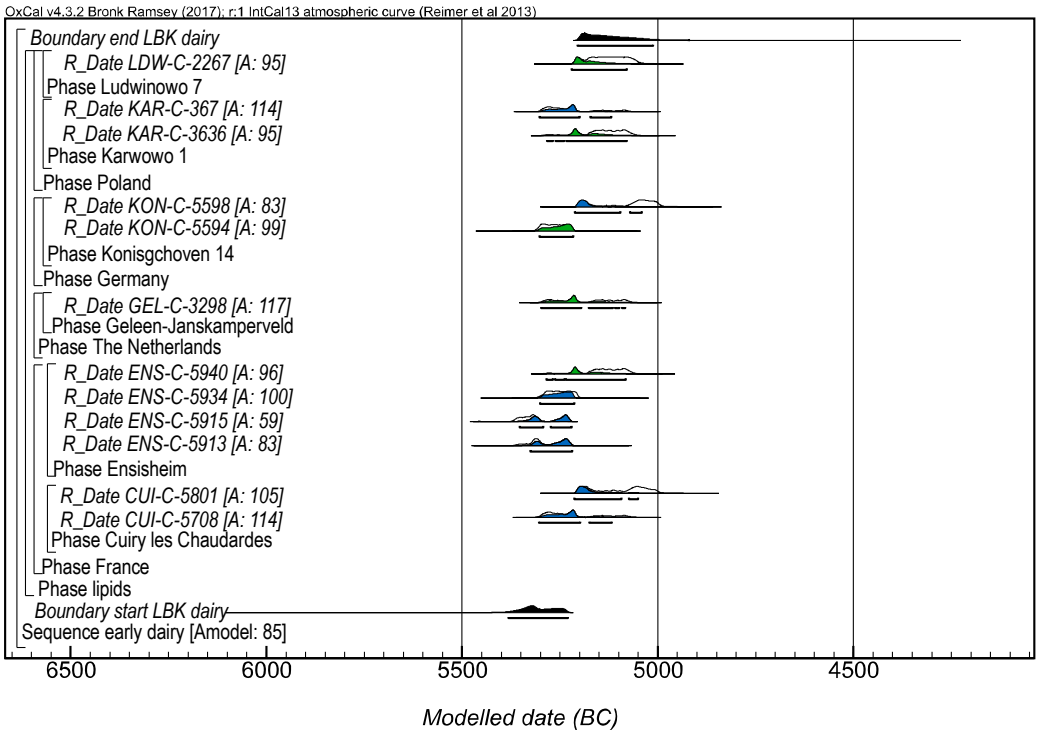

Figure 6-14: Probability distribution of radiocarbon dates on dairy residues from the LBK (in black). Plotted in blue are the probability distribution of the dates on dairy, in green on adipose fats and in outlined the simple calibration (OxCal v4.2,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

6.4.3.2 Discussion

A simple comparison of the dates from potsherds containing the earliest dairy residues with the period of use of LBK ceramics published in the literature, i.e. earliest LBK settlements in

Hungary (Jakucs *et al.* 2016), and the duration of the LBK in the Alsace region (Denaire *et al.* 2017) shows that the dates on the lipids are in good agreement with the known chronology of LBK settlements, during the 5th millennium BC. It is known that the formative LBK started during the 56th century BC and the earliest LBK settlements during the 54th century BC (Jakucs *et al.* 2016). None of the residues dated are as old as the Earliest LBK in the South-East, East and West regions (Jakucs *et al.* 2016; Figure 6-15), which seems to be in agreement with the literature as none of the Earliest LBK pottery material (phase I according to Meier-Arendt (1966) chronology) was recovered from sites where the dairy residues were radiocarbon dated. The earliest radiocarbon determinations on dairy residues dated to 5,347 – 5,303 cal BC (95 % probability) are nonetheless in agreement with the first LBK settlements from the Early LBK phase IIB (according to the Meier-Arendt (1966) and Lefranc (2007) chronology) of the Lower Alsace region, which started 5,355 – 5,240 cal BC (95% probability; Denaire *et al.* 2017). The dates obtained on dairy residues appear therefore to be in agreement with what is known from the LBK settlement and migration.

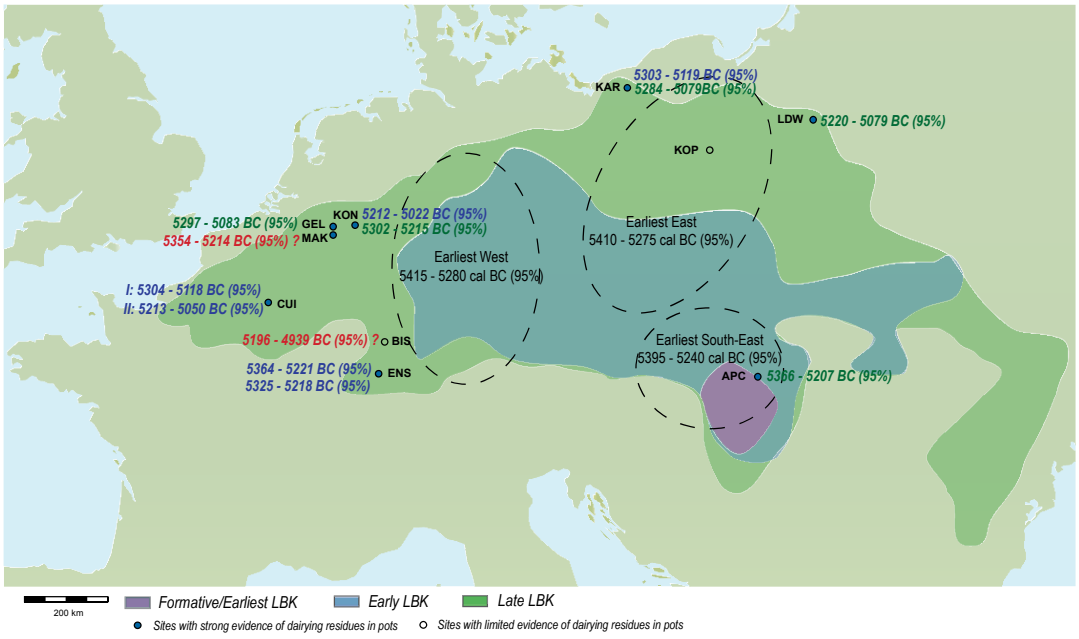

Figure 6-15: Map of LBK sites with calibrated dates on dairy. Blue dates correspond to the date on dairy residues from individual pots, red the date on dairy residue suspected to be intrusive and green the indirect dates from the same context/phase of the potsherds with early dairy at sites. The zones circled by the dashes lines correspond to the earliest settlements South-East, East and West with calibrated age associated according to Jakucs *et al.* (2016).

From the literature, the LBK began in the Hungarian region 5,395 – 5,240 cal BC (95 % probability; Jakucs *et al.* 2016). However, no sites with dairy residues from the Hungarian region were dated (due to low C recovery from the lipids in the potsherds), the only date available is an indirect one on bone collagen (OxA-25187 calibrated to 5,366 – 5,207; Jakucs *et al.* 2016), which is slightly earlier than the earliest date on dairy products obtained here, possibly suggesting that dairying activities started in Hungary with the earliest LBK settlements. Direct dates on dairy residues from Hungarian sites are, however, required to be done in future work in order to give a comprehensive picture of the joined or unrelated appearance of LBK group and dairying practices.

The earliest dates from dairy residues were obtained during the Early LBK phase in the Upper Alsace region (5,354 – 5,220 cal BC, 95 % probability; Ensisheim). The age range appears contemporaneous with the Early LBK IIB (5,355 – 5,240 cal BC, 95% probability) from the LA reinforcing once again the coexistence of the two LBK Alsatian groups, despite their likely different origin. The UA groups likely originated from the migration of Danuban groups (Hungary) toward the west, which then spread to the Paris Basin during the middle LBK phase (Jeunesse 1993a; see Chapter 5, Figure 5-1). At Cuiry-les-Chaudardes (Paris Basin) the date from dairy products (5,303 – 5,118 cal BC, 95 % probability) gave younger ages than the ones from the UA, which is in accordance with one settlement from the Middle/Late LBK only following the UA migration wave. Some reflection can be made on the migration waves from the Danube (Hungarian sites which presented dairy), to the UA and if the economy based on dairy in the UA is denoting the influence from the Earliest Danuban groups? One other possibility could be the influence on UA groups by Mediterranean cultural groups (e.g. Cardial), where an economy based on dairying appears as early as the 6th millennium BC (Debono Spiteri *et al.* 2016). These groups are known to have migrated northwards (Jeunesse *et al.* 1991). Pre-Neolithic pottery vessels from the nomadic cultural group of La Hoguette,

which shows some Mediterranean characteristics in their pottery seriation, are also commonly recovered from archaeological sites in Alsace and could be evidence for this influence (Jeunesse 1987; Pétrequin *et al.* 2009).

Even though the two Alsatian LBK groups were in contact at sites, such as Colmar (Lefranc 2007), they retained independent cultural traditions. The Lower Alsace LBK groups more likely originate from the Neckar Valley (Thévenin 1986; Jeunesse *et al.* 1991), where lipid residue results obtained from these Southern Germany sites suggest that their economies were based on meat only (Figure 6-6). Despite this, two potsherds with dairy residues were found during phase IVa1 at Bischoffsheim in Lower Alsace but the dating of one sherd with dairy suggested an intrusive material explaining such low recovery in the LA region. The LA sites show similarities with the Neckar valley in terms of an economy based mainly on meat products (unpublished data from NeoMilk database).

The sherds containing dairy lipid residues from West Rhine groups from Geleen-Janskamperveld, Netherland (5,298 – 5,084 cal BC, 95 % probability) and Konigshoven, North West Germany (5,302 – 5,216 cal BC, 95 % probability) showed similar age estimates on the earliest contexts. Dutch sites may possibly have been settled by people from the German area sites, however, this is not fully discussed in the literature (Bakels 2009). Central Germany and Bavaria, however, did not reveal intense dairying practices. The adoption of a dairying economy in the Netherlands and North-West Germany could denote, similarly to the Alsace, that the people originated from a different migration wave to the LBK groups which settled in Southern Germany.

People from Polish sites which likely originated from a Hungarian migration wave probably followed another pathway to Western LBK groups (Bogucki 1995). The site of Ludwinowo,

from the Kuyavia region, is believed to have been colonised after other regions (e.g. Lesser, Silesia) but the origins of people are not clear resulting in several hypotheses (Pyzel 2009). The prevalent hypothesis being that it is the results of several migrations from the Lesser and Silesia regions in Poland and the Carpathians Mountains in Slovakia (Pyzel 2009). The two sites of Karwowo and Ludwinowo, which were dated, showed different age ranges for the dairying activities. At the site of Karwowo (Pyrzyce region, Poland) the date from dairy residues (5,303 – 5,119 cal BC, 95 % probability) is of a similar time scale to the sites from Netherlands and North-West Germany, whereas the (indirect) dating of dairy product exploitation (5,221 – 5,079, 95 % probability) is much later at Ludwinowo (Kuyavia region, Poland), possibly relating to the later occupation of the region (Pyzel 2009). It is also possible that at Ludwinowo the population first started processing milk in sieves rather than conventional pottery vessels (Bogucki 1984; Salque *et al.* 2013; Roffet-Salque and Evershed 2015), but confirmation of this theory would require radiocarbon dating of the lipid residues from the perforated vessels.

The results from dating potsherds with dairy residues suggests that the adoption of dairy in different regions within LBK settlements was either influenced by the traditions, i.e. agricultural practices such as dairying, practised by people in the emergent regions for the LBK population (i.e. Danuban region; but not all LBK sites showed an economy with dairy) or might originate from indigenous influences from other local populations (e.g. Mediterranean influence in UA).

6.5 Conclusions

Compound-specific radiocarbon dating lipid residues was proven uniquely suited to answer questions about the validity of ORA. First, using pottery from an ethnographic context, the results of ORA with a dairy signal in clay pottery were not aberrant as they related to an historic

culture rather than the modern Samburu pastoralists. Then, at Bischoffsheim the evidence for dairying was limited, and the ^{14}C dating of one of the residues suggested that the dairy signal corresponded to a false positive result due to an intrusive material.

The data acquired here is the first attempt at radiocarbon dating the adoption of a new commodity directly from organic residue analysis of pottery. It seems that the dairying economy spread unevenly during the LBK, following different migration waves and/or different influences, through contact with other cultural groups. The start of dairying was dated from the first half of the 53rd century BC at Ensisheim in the UA region (France) and at the start of the 52nd century BC in the other sites of Cuiry-les-Chaudardes (France), Geleen-Janskamperveld (Netherlands), Konigshoven (Germany), Karwowo and Ludwinowo (Poland). This preliminary data is very promising, but the resolution obtained is quite low, as only a few dates on dairy products were available, from 8 LBK sites. More sites across the LBK settlements in Europe need to be dated, especially Hungarian sites with the earliest LBK settlements. If more radiocarbon dates were generated, mathematical simulations on the route of diffusion of dairy practices could be carried out by integrating the sum of lipid residues and archaeozoological analyses performed during the NeoMilk project, together with aDNA studies on the lactase persistence gene. This wider dating and modelling program could be the subject of another project, due to the large numbers of data needed. Nonetheless, it has been shown that the addition of a calendar age to lipid residues analysis (and other archaeological knowledge) can provide a more holistic picture of a phenomenon.

In conclusion, the possibility of CSRA lipids extracted from pottery vessels has demonstrated significant potential for dating and thus understanding important archaeological questions such as the adoption of new commodities in the diet by dating directly such residues.

Chapter 7.

CSRA of aquatic resources processing in archaeological pottery vessels

Chapter 7. CSRA of aquatic resources processing in archaeological pottery vessels

7.1 Aquatic resources in pottery vessel and marine reservoir effect

The marine reservoir effect (MRE) is a phenomenon which has to be considered in radiocarbon dating of archaeological sites located in coastal or island locations. The question of the processing of marine products in pottery vessels has already been raised in relation to the site of Cliffs End farm (Chapter 4). The potsherds radiocarbon dates were all shifted towards older values and likely affected by variable amount of marine resources raising the problem of correction of the ^{14}C measurement. It would therefore, be advantageous to correct for such MRE effects and obtain reliable dates from FAs from pottery vessels which are likely to have been influenced by a reservoir effect.

7.1.1 Detection of the exploitation of aquatic commodities at archaeological sites

There are various ways to identify the exploitation of aquatic resources in prehistory and, consequently, identify the presence of a potential MRE in radiocarbon dates, resulting from the consumption or processing of marine products. The most obvious direct evidence includes the recovery of fish bones, marine mammal bones or marine mollusc shells at archaeological sites, however, marine remains may be processed, consumed and discarded at locations away from the site (Bird and Bliege Bird 1997). In addition, fish bones are often quite small and could easily be missed during excavations or lost due to degradation (Tauber 1981). Archaeological shell middens (an accumulation of empty mollusc shells after consumption) are, however, clear proof of marine mollusc consumption or use (Roosevelt *et al.* 1991; Cramp and Evershed

2014). Technologies associated with fishing, such as harpoons or nets, also suggest the consumption of marine products at a site (Clark 1966).

Methods commonly used to investigate the importance of marine resources in the human diet include $\delta^{13}C$ and $\delta^{15}N$ analysis of bone collagen which detects enriched values in a trophic level usually related to a high protein diet (Tauber 1981; Chisholm *et al.* 1982) or the direct detection of marine fat residues in pottery vessels (Cramp and Evershed 2014). However, it should be noted that the interpretation of such results is often quite complex due to the possible consumption of a mixture of marine and terrestrial resources in the diet of past populations.

Animal (terrestrial and marine) fats can be identified by the dominance of $C_{16:0}$ or $C_{18:0}$ FAs and aquatic products can often be distinguished from terrestrial ones using specific biomarkers such as long chain DHYAs, APAAs and IFAs (Section 1.1.2; Hansel *et al.* 2004; Hansel and Evershed 2009). Such biomarkers are usually recovered in trace amount, thus, their identification can be challenging. Marine fats will typically be more enriched in ^{13}C in the major FAs in comparison to terrestrial fats with a slight overlapping of the $\delta^{13}C$ values with the non-ruminant fats (Figure 1-6; Cramp and Evershed 2014). One or more of these proxies could be used to help distinguish the possible contribution of aquatic resources.

ORA of archaeological pottery worldwide has now identified the contribution of aquatic resources to human diet, for example, in Southern Brazil, in the 10th century AD (Hansel *et al.* 2004), in South Africa during the 1st millennium AD (Copley *et al.* 2004), by hunter-gatherers and farmers in the Baltic region during the 4th, 3rd and 2nd millennium BC (Craig *et al.* 2007, 2011; Cramp *et al.* 2014b; Pääkkönen *et al.* 2018). More recently, a study of the earliest farmers of the northeast Atlantic archipelagos showed the immediate replacement of marine resources

with the adoption of intensive dairy farming, later followed by a return to exploiting marine products during the Late Iron Age and Viking/Norse eras (Cramp *et al.* 2014b).

Such previous studies have demonstrated that aquatic products are often recovered from coastal sites, showing the importance of local fauna to prehistoric populations. However, the proportion of mixed dietary components at these sites (and, consequently, inside individual pottery vessels) often remains unclear. One recent study, used cooking experiments to investigate the relationship between proportional mixes of fish and maize and at what level this would affect the freshwater reservoir offset (FRO; Hart *et al.* 2018). The study indicated that biomarkers for aquatic resources (e.g. APAAs and TMDT) might be present in the absence of a statistically significant FRO. It also indicated a that there is a high positive correlation between the percentage of C from fish in residues and FROs but, that there was no direct relationship between the percentage of raw fish cooked in a vessel and the fraction of fish C in the residue. Therefore, a statistically significant reservoir effect may occur with the fish proportion <1% of the fish/maize mix or not be significant until fish proportion is > 90 % depending on the resource processed and the ^{14}C age offset of the aquatic commodity.

7.1.2 The marine reservoir effect

7.1.2.1 Variation of the MRE

Overall, the oceans are depleted in ^{14}C relative to the atmosphere. Therefore, the organisms which live in and derive their C from ocean sources, will have an apparent age older than contemporary 'terrestrial' analogues. The marine reservoir age R(t) is defined as the difference in ^{14}C between atmospheric CO_2 and marine dissolved inorganic carbon (DIC; Stuiver *et al.* 1986). The marine reservoir effect (MRE) is on average 400 years (Stuiver *et al.* 1986) but can vary substantially. The first marine calibration curve, which dated back to 9,000 BP, was

modelled using atmospheric records to calculate the ^{14}C content in the surface layer of the ocean, according to a box diffusion model used to simulate carbon exchange between the reservoirs (Oeschger *et al.* 1975; Stuiver *et al.* 1986). In addition, new marine calibration curves, which date to 50,000 BP, also integrate radiocarbon and uranium/thorium analyses on sea corals (Hughen *et al.* 2004; Reimer *et al.* 2009; 2013).

The ^{14}C content of the marine reservoir is time and location dependent, resulting in regional and temporal offsets. This is defined using the term ΔR, which is the difference between R(t) measured in a specific area and the modelled age using the marine calibration curve (Stuiver *et al.* 1986). The local variation at the time, ΔR, needs to be considered when studying an archaeological site with a possible marine influence (Cook *et al.* 2015).

Usually, open coastal locations are believed to be well-mixed and would give a homogenous distribution of C in the water, as opposed to restricted environments such as fjords which could prevent a good mixing of C in the surface ocean and thus lead to a significant difference in ΔR (and apparent MRE to marine organism living in such areas) to the regional one (Heier-Nielsen *et al.* 1995; Cage *et al.* 2006; Ascough *et al.* 2009). Furthermore, the introduction of terrestrial detritus or geological material which can locally affect the reservoir, e.g. peatland, estuarine or volcanic areas, must also be taken into account (Spiker 1980; Dye 1994; Hogg *et al.* 1997; Ulm 2002). Such reservoir effects are distinct from the MRE and must be considered separately (Alves *et al.* 2018). Some authors have suggested that MREs can also be species dependent in the same environment based on their food sources (Forman Steven and Polyak 1997; Hogg *et al.* 1997), however, such variation between species may not necessarily be visible (e.g. Ascough *et al.* 2005b; Russell *et al.* 2011). In addition, fish, as opposed to molluscs, are mobile during their lifetime, and could quite easily move away from their point of origin, presenting an apparent age which does not necessarily correspond to their recovery location

but to the average of other locations (Russell *et al.* 2011). These studies all emphasise the complexity of the MRE, largely due to spatiotemporal variations.

The 'best practice guidelines' to use when dealing with the MRE, as recommended by Cook *et al.* (2015), suggest using the latest marine calibration curve available, a ΔR value appropriate for the spatiotemporal area studied and to ensure that this ΔR value and error associated is pertinent when calibrating marine samples.

7.1.2.2 Methods to measure local variations in MRE

Ascough *et al.* (2005a) proposed 3 approaches to determine the local variation to the MRE:

(i) The use of materials with a known calendar age. This consists mainly of specimens from museum collections which were collected whilst alive, thus having a documented calendar age. However, materials from the late 19th century onwards are unusable (or will require correction) due to the Suess effect and nuclear weapons testing in the 1950s which affected the ^{14}C rate in the atmosphere.

(ii) The use of tephra (volcanic matter ejected during an eruption) from the same layer both deposited at sea and on land at the same time. The dating is performed on materials extracted from sediments (e.g. foraminifera, molluscs shells or plant materials). Such dating would, however, be influenced by the accumulation rate of sediments and limited to time and locations where there are large tephra deposits.

(iii) The use of same age terrestrial and aquatic organisms i.e. deposited at the same time. This approach, referred to as "paired measurements", requires sampling short-lived aquatic and terrestrial samples from undisturbed archaeological contexts. In practice,

shells are preferable to fish, due to their short lives, and their restricted immobility is considered representative of surface coastal water. However, determining the environment that the shells originate from is important as it can be influenced by different reservoir effects in restricted areas where the mixing of water, and thus C, is not homogenous (e.g. Heier-Nielsen *et al.* 1995).

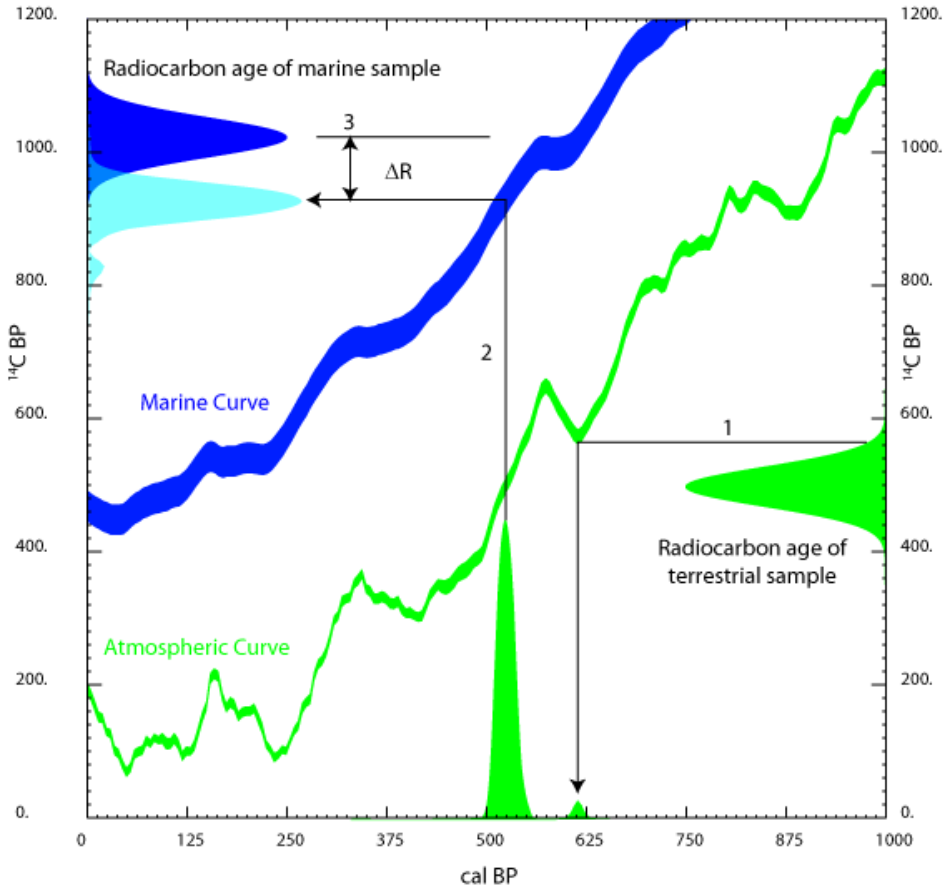

Figure 7-1: Theoretical approach to estimate local variation to the marine reservoir effect using paired terrestrial/marine samples. From Stuiver *et al.* (2018)

Approach (iii), using pairs of terrestrial/aquatic samples from the same context, was adopted in this thesis. In practice, this involves calibration of the terrestrial dates using the atmospheric calibration curve, then converting the calendrical date to a theoretical marine age using the marine calibration curve. The age difference between the modelled marine value to the measured age of the aquatic organism corresponds to ΔR (Figure 7-1). Multiple measurements

are required to have an accurate estimation of the reservoir effect at the site (Ascough *et al.* 2005a).

7.1.2.3 Calibration of dates from bone collagen for animals consuming mixed marine/terrestrial diets

When dating archaeological bone collagen some organisms dated will have taken up carbon from both terrestrial and marine sources. This is especially the case for coastal and island dwelling humans (and other omnivores, e.g. pigs and dogs) who are likely to consume fish and other seafoods, alongside terrestrial animal products. This complicates calibrations which require the use of both marine and terrestrial curves (e.g. *Mix_Curves* function in OxCal program; Bronk Ramsey 2009). The two calibration curves are mixed based on the percentage and error associated of marine C present in the sample, therefore, before any MRE correction, an appropriate estimate of the terrestrial/aquatic resources mixing has to be carried out. Such corrections also include ΔR calculation at the site for calibration against the marine curve (Cook *et al.* 2015; Reimer *et al.* 2013).

The contribution of marine food to the diet can be estimated from bulk $\delta^{13}C/\delta^{15}N$ isotope analyses (Cook *et al.* 2015). However, this can be complex. Usually, enriched $\delta^{13}C$ and $\delta^{15}N$ values provide information about the trophic level and a protein-rich diet related to the marine food contribution and, as such, the percentage can be calculated using a linear mixing relationship (Cook *et al.* 2015). However, a low protein diet with low $\delta^{13}C$ value will not solely reflect a terrestrial diet as high proportions of marine food can still give depleted isotope values (Bonsall *et al.* 2009). Therefore, for calibrating dates from mixed marine/terrestrial samples, Cook *et al.* (2015) made several recommendations; (i) obtain information on diet from the archaeozoological remains and plant/grain residues at the archaeological site, (ii) obtain an

estimation of the percentage of the diverse terrestrial resources consumed, which corresponds to measuring the stable isotope ratios on collagen and modern equivalent food sources to obtain end-member $\delta^{13}C$ values, (iii) obtain a estimation of the percentage of the diverse marine resources consumed and then measure the end-member $\delta^{13}C$ values from modern analogues. However, these data are not necessarily accurate and are more of a semi-quantitative estimate, due to the difficulties in obtaining information on the diet and obtaining appropriate references animals, since the latter could be influenced by modern feeding practices (e.g. Roffet-Salque *et al.* 2016).

A number of studies have applied such mixing curves to calibrate dates on human collagen; such as Viking populations who are well-known for their seafood consumption (Arneborg *et al.* 1999; Jarman *et al.* 2018). One recent study, focused on the skeleton, excavated during the construction of a car park in Leicester, believed to be that of Richard III (Cook *et al.* 2015). The radiocarbon date from the skeleton exhibited older dates than the known age of his death, however, enriched $\delta^{13}C$ and $\delta^{15}N$ values on the bulk collagen suggested a significant contribution of marine products to the diet. End-members for the two possible sources of food in his diet could not be calculated, thus, arbitrary average values and uncertainties for pure terrestrial and marine were applied to calculate the dietary marine percentage. After correction, using a literature ΔR value for medieval Britain, the calibrated date range agreed with the date of death of Richard III, supporting the hypothesis of this skeleton to potentially be the one of the past kings of England. This demonstrated that approximations are required in some cases as it is not always possible to calculate an accurate proportion of fish in the diet or the local MRE.

7.2 Aims and objectives

In the previous chapters, all the sherds which were dated came from inland locations (with the exception of Cliffs End Farm) and the technique of CRSA dating of lipids was proven valid for a range of ages and inland locations. However, the protocol has yet to be tested on sherds from a coastal environment, where it is likely that the consumption of aquatic resources might be of importance in the local diet. At such sites, the problem of a possible MRE is likely to occur, meaning that corrections would be required for such ^{14}C measurements. The possible mixing of marine and terrestrial commodities should also be considered as it would increase the complexity of correction of ^{14}C dates. This raises the question whether correction for the reservoir effect in pottery vessels is possible? In addition, it is known the modern abundance of $C_{16:0}$ and $C_{18:0}$ FAs differ for terrestrial and marine organisms and their mixing is not necessarily linear (Mukherjee *et al.* 2005). This raises of question of whether the apparent individual FAs show both the same proportion of marine and terrestrial fats and whether the internal criterion on the two FAs introduced in Chapter 4 would remain valid? Certainly, two different apparent ages for the $C_{16:0}$ and $C_{18:0}$ FAs is perfectly feasible, as the result of mixing fresh fats or oils of marine and terrestrial origin where latter FAs had different abundances in the parent material.

The aim of this chapter was to undertake radiocarbon dating of pottery vessels from a coastal site in order to understand the influence of aquatic resources on CSRA dating of lipids from pottery and also to correct for such effects. The work undertaken included: (i) lipid residue and stable isotope analysis to select pottery vessels for ^{14}C dating, (ii) calculation of the local reservoir effect using paired marine and terrestrial animal remains, (iii) using a multiproxy approach (i.e. biomarkers, stable isotopes and ^{14}C dates) to evaluate the proportion of mixing

of marine and terrestrial lipids, and (iv) application of the relevant marine reservoir corrections to dates obtained from lipids.

7.3 Dietary practices at the archaeological site of Bornais

7.3.1 Site description

7.3.1.1 Settlement and chronology

The site of Bornais is located in Western Isles of Scotland (South Uist, Outer Hebrides, UK; Figure 7-2; Appendix 9.1). The site comprises of 4 mounds, excavation of which revealed a long period of habitation from the late Iron Age to the Norse (Viking Age and early Medieval) period (Sharples forthcoming).

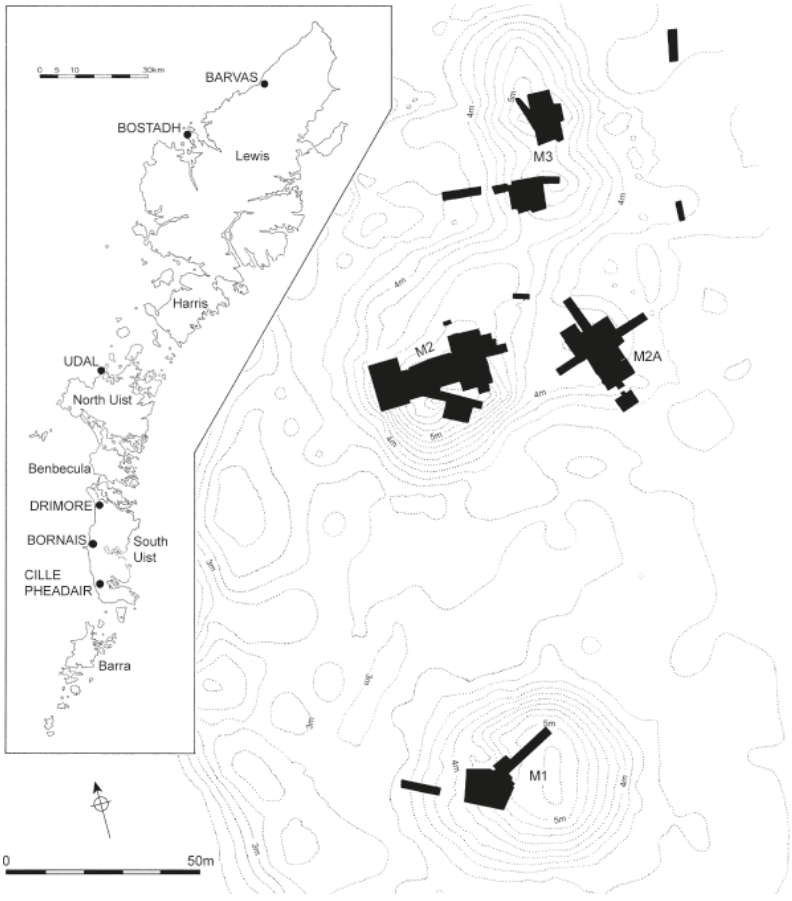

Figure 7-2: Location of the site of Bornais and the 4 mounds excavated. From Sharples *et al.* (2016), Figure 17.1.

A total of 109 materials were previously submitted for radiocarbon analysis from Mound 1 (33 dates), Mound 2 (36 dates), Mound 2A (27 dates) and Mound 3 (11 dates). The radiocarbon dates were obtained from carbonised seeds, cattle, sheep, red deer, pig and human bones. Bulk stable carbon isotope analysis of the same collagen extracts suggested the consumption of a predominantly C_3 diet, appearing to rules out the possibility of a reservoir effect (Marshall 2005, 2016, forthcoming).

The late Iron Age (LIA 1 and 2) occupation started during the 5th-6th century AD and ended in the 8th millennium AD. There then appears to be a hiatus in the settlement before the construction of the first Viking house in the mid-9th century AD. The Norse period comprises 3 phases [Early Norse (EN), Middle Norse (MN) and Late Norse], ending during the 14th century AD.

7.3.1.2 Economy

Cereals were produced at the site with a predominance of oats and barley over flax and rye. An intensification in agriculture occurred from the LIA to Norse period (Sharples *et al.* 2016). The faunal assemblage was particularly rich in diversity with terrestrial animals (e.g. dog, red deer, roe deer and otter), small vertebrates, birds (e.g. gull, cormorant, goose and duck) and marine animals (Sharples *et al.* 2016; forthcoming). The main domesticated animal species, corresponding to ~ 90 % of the faunal assemblage, comprised cattle, sheep and pigs (Sharples *et al.* 2016). The proportion of pigs at the site increased during the EN period (but remained low compared to the ruminant animals) together with an increase in the importance of sheep over cattle with time. The reconstruction of the kill-off pattern of sheep suggested a herd management strategy predicated on milk products. The mortality profile of cattle differed from the LIA to the Norse activities, with a herd profile suggesting dairying in the later period. Stable

isotope analysis on the faunal assemblage suggested the grazing of cattle and sheep on a pure C_3 diet, whereas, $\delta^{13}C$ and $\delta^{15}N$ values from the pigs, red deer, dogs and birds suggests they subsisted on both the marine and terrestrial resources (Jones *et al.* forthcoming).

Fish bones and mollusc shells (limpets and winkles) are particularly abundant at the site and a limited quantity of marine mammal bones (seal) were also found. Salmonids and saithe were found in the earliest settlement levels, whereas the Norse settlement contained numerous herring remains (Sharples *et al.* 2016). Overall, at Mound 2 and 2A, a wide range of fish (eel, saithe, cod, haddock, ray, turbot, mackerel etc) was identified. Interestingly, entire fish remains were recovered in the LIA contexts suggesting processing at the site, whereas in the Norse settlement mainly vertebrae were recovered, suggesting that fish were processed in another location and arrived ready for consumption (Sharples *et al.* 2016).

7.3.2 Lipid residue analysis at the site

Lipid residues analyses were previously performed on 131 potsherds from all the phases and mounds at the site (Cramp forthcoming). At the time of sampling, the site was still being excavated and the contexts were not necessarily well-dated afterwards. As part of this thesis, an additional 49 pottery vessels and 8 visible residues associated with house 2 at Mound 2 (well-dated floor plan from which ~3,000 sherds were recovered, Appendix 10.1) were analysed by ORA.

7.3.2.1 GC and GCMS analyses

Total lipid extracts with concentrations >5 $\mu g.g^{-1}$ were recovered from 96 % (n = 47) of the 49 potsherds from House. These had an average lipid concentration of 1.2 $mg.g^{-1}$ (Appendix 8.2). The majority of the TLEs (83 % (n = 35) of the sherds and those of 4 visible

residues were dominated by the $C_{16:0}$ and $C_{18:0}$ fatty acids characteristic of degraded animal fats (Figure 7-3). The odd-carbon numbered $C_{15:0}$ and $C_{17:0,}$ fatty acids, including *iso*- and *anteiso*-isomers, possibly indicative of microbial activity in the rumen and, hence, characteristic of a ruminant product origin, was also present (Keeney *et al.* 1962).

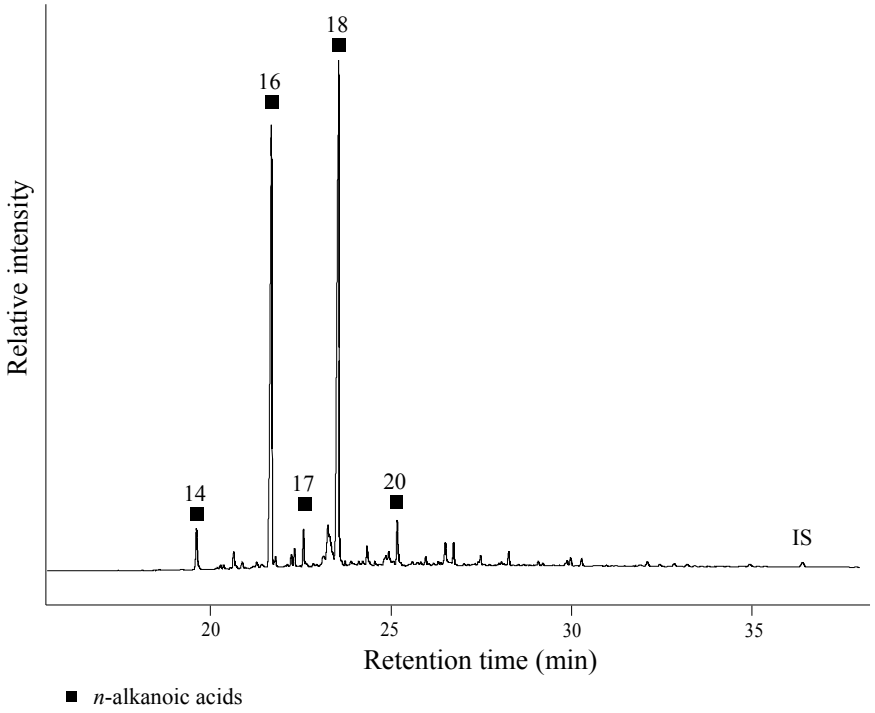

Figure 7-3: Partial gas chromatogram of sample BN-173 showing a FA distribution typical of a degraded animal fat. The black squares correspond to FAs and the numbers represent the carbon chain length of the biomarkers. IS is the internal standard.

Many of the TLEs (63 %; $n = 22$ of the sherds with residues) exhibited marine biomarkers. The long-chain DHYAs ($C_{18,}$ C_{20} and C_{22}) were detectable in 34 % ($n = 12$) of the sherds producing residues and three of the visible residues (Figure 7-4a). Long-chain APAAs ($C_{18,}$ C_{20} and C_{22}) were recovered from 31 % ($n = 11$) of sherds with residues and from four visible residues (Figure 7-4b). However, both DHYAs and APAAs were only present in two sherds and one visible residue. This may be due to the degradation of the DHYAs occurring at the high temperatures required (>270 ºC; Hansel *et al.* 2004) to form APAAs. The IFAs (phytanic acid and especially TMTD) were recovered in 40 % ($n = 14$) of sherds with residues and four visible.

The TMTD was only detected in extracts of sherds that contained either the DHYAs or the APAAs, with one exception. In total, only 4 % (n = 2; BN-140, BN-173 and visible residue BN-149VR) of the potsherds with lipid residues contained all 3 classes of aquatic biomarkers, 21 % (n = 10) 2 aquatic biomarkers and 47 % (n = 22) showed one aquatic biomarkers.

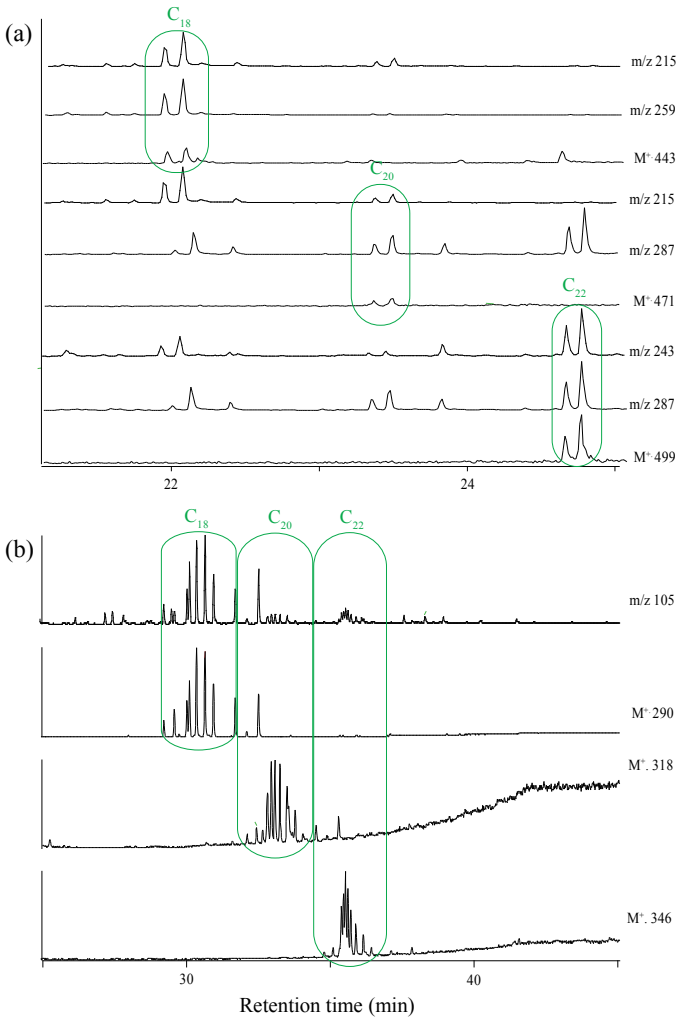

Figure 7-4: Mass chromatograms of BN-173 (a) obtained from GC-MS SIM analysis of the TLE on a non-polar column, showing identification of the C_{18}, C_{20} and C_{22} DHYAs, (b) analyses on a polar column showing identification of the C_{18}, C_{20} and C_{22} APAAS according to Cramp and Evershed (2014).

The remainder of the TLEs (n = 13 of the sherds with residues) did not contain any aquatic biomarkers. Those sherds did comprise either the C_{18} DHYA, C_{18} APAA and/or the phytanic acid, which, by themselves, are not characteristics of aquatic products, therefore these cannot be considered as of marine origin.

Both visible and absorbed lipid residues of the same potsherds showed similar ORA results (presence or absence of aquatic biomarkers) except for potsherd BN-167 which showed aquatic biomarkers in the absorbed residue but not in the visible residue, while for potsherd BN-176 the reverse was the case.

7.3.2.2 Stable carbon isotope analyses

The $\delta^{13}C$ values of the palmitic and stearic acids were determined by GC-C-IRMS in order to identify the sources of the animal products extracted from 40 potsherds (Figure 7-5a). Significantly, the $C_{16:0}$ and $C_{18:0}$ fatty acids displayed $\delta^{13}C$ values characteristic of mixtures between ruminant and marine/porcine products (Copley *et al.* 2004; Cramp and Evershed 2014). Only one data point falls in the reference ellipse of ruminant adipose fats (Figure 7-5a). The extract yielding the most enriched carbon values also containing aquatic biomarkers, strongly suggest the use of marine products rather than porcine. A number of TLEs exhibiting enriched $\delta^{13}C$ values, show no detectable aquatic biomarkers, possibly due either to the processing of pig products (pig bones are present in the faunal assemblage but in a relatively low proportion) or the processing of marine commodities under conditions that did not result in the formation of marine biomarkers. A total of 22 sherds showed $\Delta^{13}C$ values below -3.1 ‰ which supports the hypothesis of some mixing of dairying products with either marine or porcine products. The other sherds with less depleted $\Delta^{13}C$ values showing values >-3.1 ‰ could result from the mixing of ruminant carcass with marine or porcine products.

The surface and absorbed residues from the same sherds gave different $\delta^{13}C$ values varying by 0.5 to 3.8 ‰ (BN-167 being the highest) with an average of 1.8 ‰. The largest differences likely relate to the presence of a greater abundance of aquatic lipids in adsorbed residue (more enriched values) compared to the surface residues. The smaller differences seen for the other

potsherds (over the accepted instrumental error of 0.3 ‰) could support the interpretation that the surface and adsorbed residues relate to different cooking events or, that the amount of C from aquatic resources taken in the food crust and the absorbed residues differ (Hart *et al.* 2018).

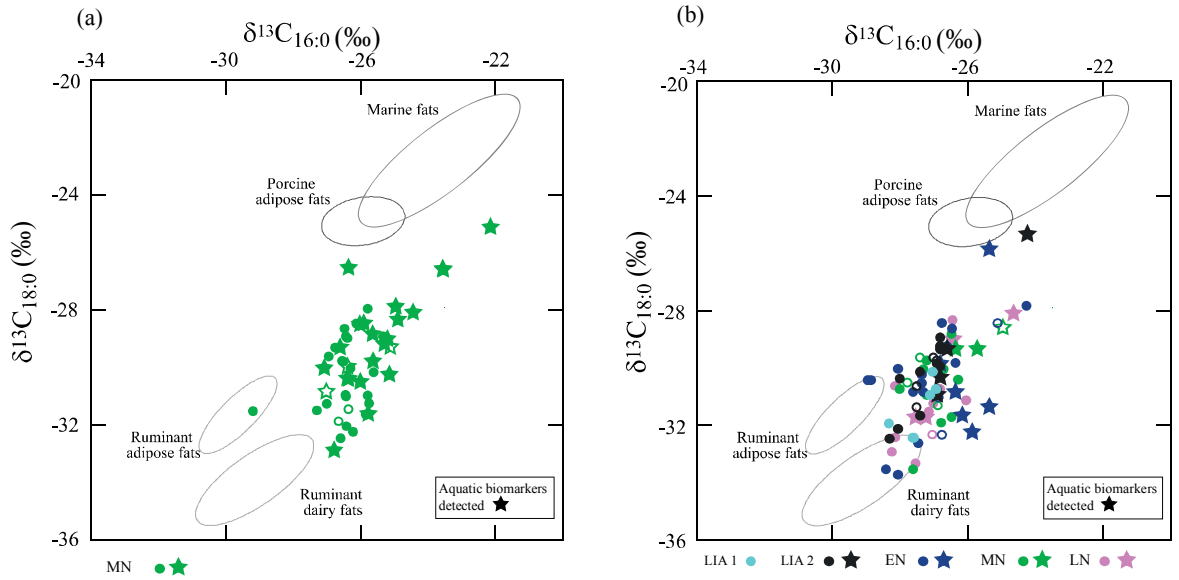

Figure 7-5: Scatter plots of $\delta^{13}C_{18:0}$ plotted against $\delta^{13}C_{16:0}$ at the site of Bornais for potsherd TLEs from (a) Mound 2, House 2 analysed in this thesis, and (b) in the study of Cramp (forthcoming). Data points are: filled circles to the absorbed residues, open circles to the visible residues, and stars correspond to sherds which contained aquatic lipid biomarkers. Ellipses correspond to the range of the modern references animals (Copley *et al.* 2003; Cramp and Evershed 2014).

7.3.2.3 Comparison with previous ORAs at the site

Lipid residue results obtained by Cramp *et al.* (2014b, forthcoming) used chloroform/methanol extraction (Evershed *et al.* 1990) yielded an average lipid concentration of 95 $\mu g.g^{-1}$. The new results obtained in this thesis for pottery from House 2 used the more recently developed acidified methanol, and likely accounts for the higher lipid recoveries (Correa-Ascencio and Evershed 2014). The $\delta^{13}C$ values obtained from the $C_{16:0}$ and $C_{18:0}$ FAs from pottery from both the LIA and Norse phases, suggest a dominance of dairy and ruminant carcass product processing, as well as some mixing of non-ruminant and marine products (Copley *et al.* 2004;

Cramp and Evershed 2014; Figure 7-5b). Only the pottery from phase 1 from the LIA 1 lacked aquatic biomarkers.

7.3.3 Discussion and selection of potsherds for ^{14}C dating

Lipid residue analysis of potsherds from Bornais supports the exploitation of aquatic resources at the site, together with dairy products. Most of the carbon isotope values, however, are shifted along mixing lines, suggesting the mixing of meat, dairy and aquatic lipids in the same vessels. Lipid recovery from these potsherds contained abundant evidence for aquatic products, suggesting that these pottery vessels would suitable candidates for ^{14}C dating and testing of the CSRA method on mixed terrestrial and marine profiles. A total of 22 potsherds containing no aquatic biomarker or at least one class (from Mound 2) were selected for CSRA (Figure 7-6).

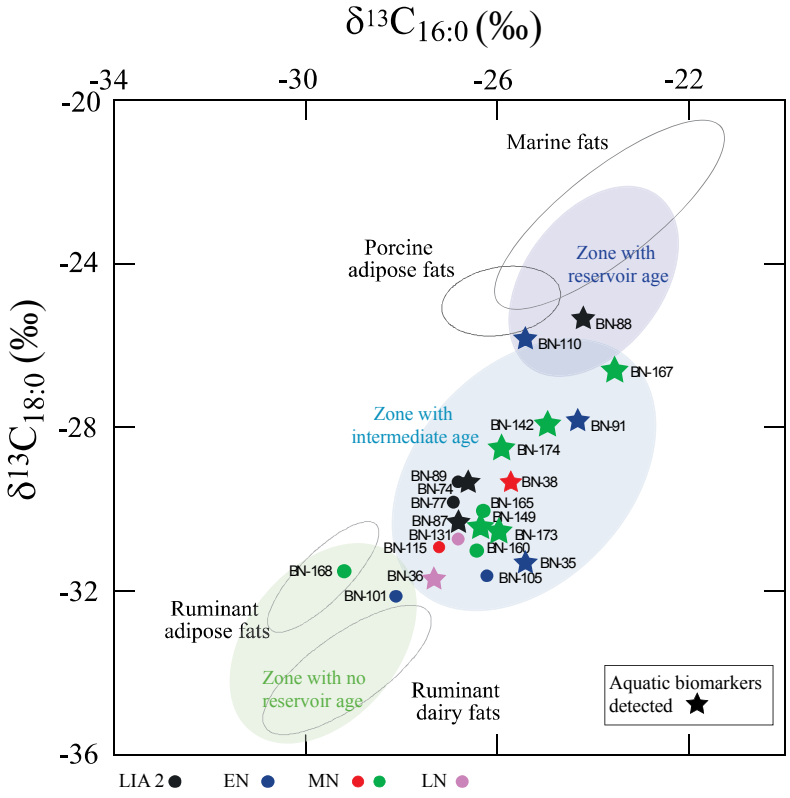

Figure 7-6: Scatter plot of $\delta^{13}C_{18:0}$ plotted against $\delta^{13}C_{16:0}$ for the 22 potsherd extracts selected for ^{14}C dating by CSRA. Shading indicates the area of the plot where lipid residues are hypothesised to be affected to varying degrees by the MRE.

The sample selection allows investigation of whether: (i) all sherds containing aquatic biomarkers will exhibit a reservoir effect, (ii) there is a relationship between the measured radiocarbon age and enriched stable carbon isotope values due to the mixing of both meat/milk and marine products, (iii) sherds lacking aquatic biomarkers will show a reservoir effect, especially the ones exhibiting enriched $\delta^{13}C$ values, (iv) if the percentage of marine resources processed in pots can be estimated, and (v) compound-specific radiocarbon dates can be corrected for the MRE.

7.4 Calculation of the local reservoir effect at Bornais

7.4.1 Radiocarbon dating of mollusc shells, fish and terrestrial animal bones

Radiocarbon dates for terrestrial and marine remains, from the same contexts as the pottery vessels selected for dating based on their ORA results, were generated as part of this thesis to allow calculation of the MRE for the relevant contexts. Figure 7-7 reports the relative stratigraphy at Mound 2 (Sharples forthcoming).

Firstly, pottery vessels from 3 contexts of the LIA 2 period were selected. Context BAC corresponds to infill layers above a floor layer, BAF to layers under the central house and context BAG is from cut and fill between the LIA 2 and EN periods, which ^{14}C dates (see Section 7.4.1.1) place in the LIA 2 period. For the EN phase, the contexts BBA and BBD correspond, respectively, to the foundation and abandonment of House 1 (Appendix 9.1). Similarly, the contexts BCA and BCC of the MN phase correspond to the foundation and abandonment of House 2 and the AD context corresponds to the infilling of an ancillary structure. Finally, the context AG from the LN period corresponds to the infilling of house AE.

When possible, for each period and layer, at least two terrestrial and two marine samples (shells or fish bone) were subjected to ^{14}C dating (Sections 2.3.4.6, 2.3.4.6, 2.4.8, 2.4.9, 2.5.3.6). In total 11 limpets, 4 winkles, 13 fish bones 10 terrestrial animal bones were selected for dating. A further 7 radiocarbon dates (BCC context) were previously available (Marshall *et al.* forthcoming).

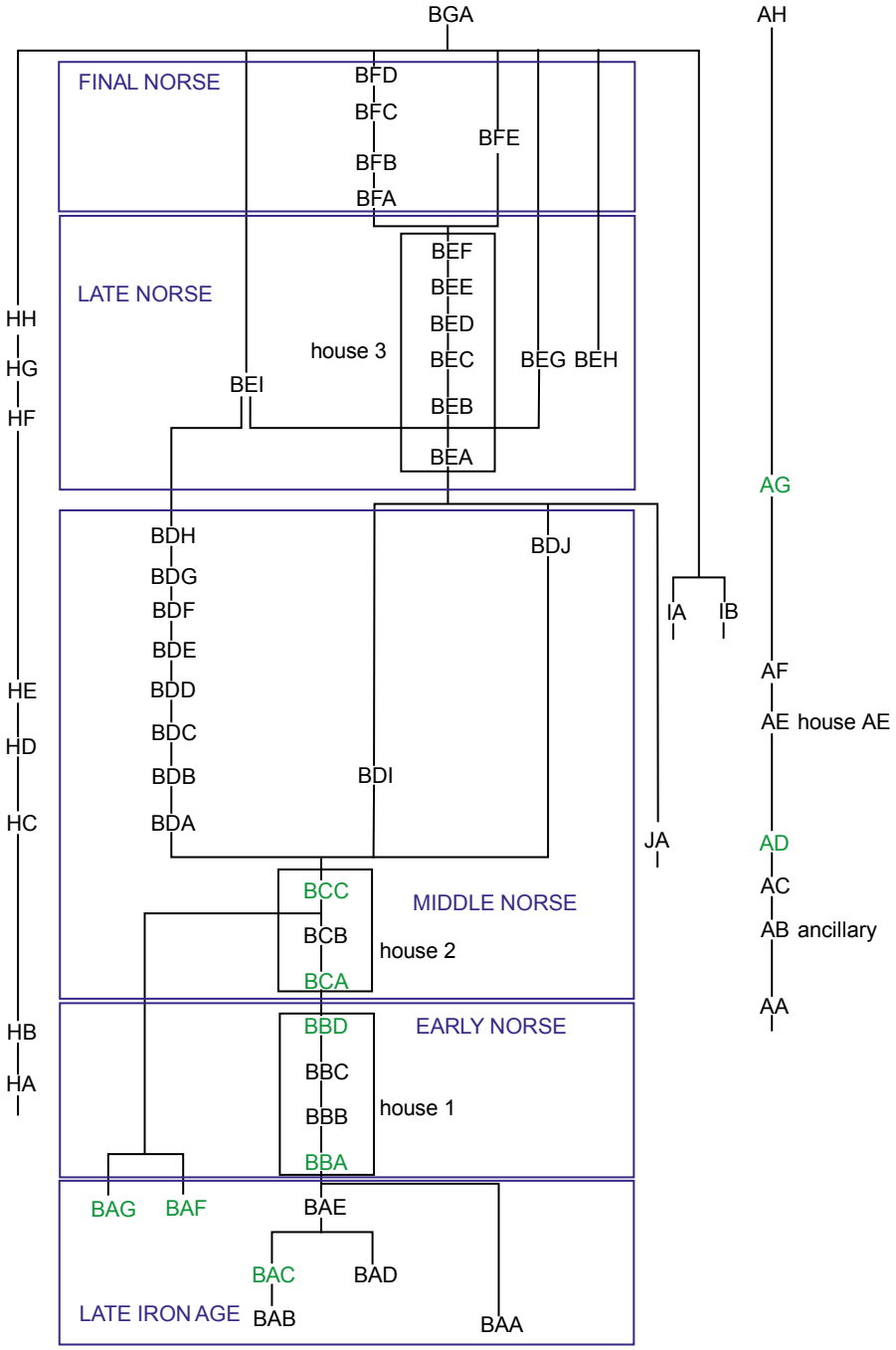

Figure 7-7: Schematic diagram showing the stratigraphic information for the Mound 2. Green contexts correspond to the ones studied in this thesis. Courtesy of N. Sharples.

7.4.1.1 Radiocarbon dating terrestrial animals

The results from terrestrial animal bones are reported in Table 7-1. Six terrestrial animal bones were dated from the LIA 2 period and the dates passed the χ^2 test at the 5 % level (T' = 11.0, T'(5 %) = 11.5, υ = 6). The layer BAC was dated from three bones, which when combined gave a date of 1,275 ± 12 BP (T' = 1.3, T'(5 %) = 6.0, υ = 2), the layer BAG dated from two bones which gave a combined date of 1,320 ± 18 BP (T' = 0, T'(5 %) = 3.8, υ = 3), whereas layer BAF was dated only by one collagen extract, to 1,348 ± 25 BP.

Layer BBD, from the EN period, showed two dates on animal bone which failed the χ^2 test at the 5 % level (T' = 15.0, T'(5 %) = 3.8, υ = 1), but this could reflect a long settlement period of House 1 (Marshall *et al.* forthcoming).

The seven animal bones dated in the MN period (averaged to 955 ± 11 BP), from layer BCC (House 2, previously dated; Marshall *et al.* forthcoming) do not pass the χ^2 test at the 5 % level (T' = 20.9, T'(5 %) = 14.1, υ = 6), however, this could reflect a long occupation period for House 2 (Marshall *et al.* forthcoming). With the removal of two potential outliers (SUERC-22894 and SUERC-22890) the remaining dates passed the χ^2 test at the 5 % level (T' = 6.6, T'(5 %) = 7.8, υ = 4).

The layer AD was only dated by one bone collagen sample, to 956 ± 25 BP (BN-MB9), which falls in the range of age of the other MN period dates (T' = 6.7, T'(5 %) = 12.6, υ = 5).

The layer AD from the LN period was dated to 930 ± 25 BP (BN-MB7) based on one collagen extract.

Table 7-1: Radiocarbon dates on charred grain and terrestrial animal bone collagen for the same contexts of the potsherds dated (OxA/SUERC data from Marshall *et al.* forthcoming) * refer to statistical outliers.

Sample	Phase	Layer	Context	Lab #	$F^{14}C \pm 1\sigma$	Age ± 1σ BP	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Description
BN-MB-3	LIA 2	BAC	[1913]	BRAMS-1710.1.1	0.8535 ± 0.0026	1,272 ± 25	-21.8	4.9	Cattle 1st phalanx (nenoatal) unfused
BN-MB-4	LIA 2	BAC	[1913]	BRAMS-1711.1.1	0.8508 ± 0.0026	1,298 ± 25	-20.7	4.8	Caprine mandibula
BN-MB-6	LIA 2	BAC	[1917]	BRAMS-1713.1.1	0.8550 ± 0.0026	1,258 ± 25	-20.7	4.5	Animal bone; unidentified
				BRAMS-1713.2.1	0.8544 ± 0.0026	1,264 ± 25	-	-	Duplicate BN-MB-6
BN-MB-5	LIA 2	BAF	[2626]<11378>	BRAMS-1712.1.1	0.8455 ± 0.0026	1,348 ± 25	-20.5	7.1	Pelvis (pallium; maybe cattle < 1 y)
BN-MB-1	LIA 2	BAG	[1075] 2949	BRAMS-1708.1.1	0.8485 ± 0.0026	1,320 ± 25	-20.6	4.2	*Bos* taurus metapodia condylis unfused
BN-MB-2	LIA 2	BAG	[1075] 2949	BRAMS-1709.1.1	0.8484 ± 0.0026	1,320 ± 25	-20.3	4.5	Cattle 1rst phalanx (nenoatal) unfused
BN-MB-8*	EN	BBD	[43]	BRAMS-1715.1.1	0.8740 ± 0.0026	1,082 ± 25	-21.4	7.6	*Bos taurus* metapodia condylis
BN-MB-10*	EN	BBD	[43]	BRAMS-1719.1.1	0.8890 ± 0.0027	945 ± 25	-20.5	4.7	Mammal cranium
-	MN	BCC	[1010] <9684>	SUERC-2684	-	925 ± 35	-21.7	4.2	*Bos* thoracic vertebra
-	MN	BCC	[1049] <9809>	SUERC-22894*	-	875 ± 30	-21.9	9.6	*Cervas*; radial, intermediate & magnum carpals
-	MN	BCC	[1267] <9457>	SUERC-22890*	-	1,035 ± 30	-18.3	10.6	*Sus*; lateral metapodial, 2x phalange
-	MN	BCC	[1231] <9496>	GU-18290	-	-	-	-	Carbonised *Cerastium* sp.
-	MN	BCC	[1057] <9895>	SUERC-22896	-	970 ± 30	-21.3	7.3	*Bos*; radial, intermediate, uniform carpals
-	MN	BCC	[2297]<11316>	SUERC-22897	-	975 ± 25	-210	5.5	*Bos*; radial, ulnar, intermediate, pisiform carpal
-	MN	BCC	BO99/8152/182	OxA-15420	-	903 ± 27	-20.5	3.4	*Ovid*
-	MN	BCC	BO99/8155/557	OxA-15522	-	985 ± 26	-21	9.6	*Bos*
BN-MB-9	MN	AD	[69]	BRAMS-1716.1.1	0.8878 ± 0.0026	956 ± 25	-20.6	5.5	*Bos taurus* metatarsal
BN-MB-7	LN	AG	[58]	BRAMS-1714.1.1	0.8907 ± 0.0026	930 ± 25	-17.1	11.0	Medium mammal lumber vertebrate (sheep)

7.4.1.2 Radiocarbon dating fish bones and mollusc shells

Both fish bones and marine mollusc shells were sampled and, when possible, examples of both were dated for each site layer (Table 7-2).

The LIA 2 period, from context BAC, showed consistent ^{14}C age determinations on the four limpet shells, which gave an average date of 1,627 ± 23 BP (T' = 0.5, T'(5 %) = 7.8, υ = 3). The two limpets dates from the BAF layer were statistically identical (T' = 0.3, T'(5 %) = 3.8, υ = 1) and averaged to 1,575 ± 18 BP, whereas the fish bones showed high variability (T' = 121.7, T'(5 %) = 3.8, υ = 1) which could reflect the mobility of the species (Russell *et al.* 2011) or intrusive/residual samples. Context BAG was dated to 1,509 ± 25 BP (BN-F-1) by one fish bone. The EN period was dated by one marine organism to 1,622 ± 26 BP (BN-L-7).

With regard to the MN period, despite all the dated materials being found in the same context, (meaning they are contemporaneous), the dates for layer BCC, which originate from fish bones, limpets and winkles, show 3 distinct age groupings (Figure 7-8). The shells can be separated into two groups; Group (a) comprises one limpet and two winkles (BN-L-10, BN-L-11, BN-W-1 and BN-W-3) dated, on average, to 1,249 ± 12 BP (T' = 0.8, T'(5 %) = 5.9, υ = 2) and Group (b) comprises two limpets and two winkles (BN-L-9, BN-W-2 and BN-W-4), dated, on average, to 1,599 ± 12 BP (T' = 1.8, T'(5 %) = 7.8, υ = 3). Only the limpet BN-L-8 showed an age distinguishable from Groups (a) and (b) and could therefore be an outlier. The fish bones (Group (c)) passed the χ^2 test at the 5 % level (T' = 3.7, T'(5 %) = 9.4, υ = 4) and are dated, on average, to 1,324 ± 11 BP. The homogeneity of ages within the 3 distinct groups supports that various offsets (MRE and maybe freshwater) affect the marine species at the sites.

Table 7-2: Radiocarbon dates on fish bones, limpets and winkles from the contexts of the pottery vessels dated in this thesis. * refer to statistical outliers

Sample	Phase	Layer	Context	Lab #	$F^{14}C \pm 1\sigma$	Age ± 1σ BP	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Description
BN-L-1	LIA 2	BAC	[1913] <10735>	BRAMS-1727.1.1	0.8169 ± 0.0026	1,624 ± 26	-	-	Limpet
BN-L-2	LIA 2	BAC	[1913] <10735>	BRAMS-1728.1.1	0.8167 ± 0.0026	1,627 ± 26	-	-	Limpet
BN-L-5	LIA 2	BAC	[1917] <10724>	BRAMS-1731.1.1	0.8151 ± 0.0026	1,642 ± 26	-	-	Limpet
BN-L-6	LIA 2	BAC	[1917] <10724>	BRAMS-1732.1.1	0.8178 ± 0.0026	1,616 ± 26	-	-	Limpet
BN-F-9*	LIA 2	BAF	[2626]	BRAMS-1725.1.1	0.8143 ± 0.0025	1,651 ± 25	-11.2	10.7	Fish bone, spine
BN-F-10*	LIA 2	BAF	[2626]	BRAMS-1726.1.1	0.8512 ± 0.0026	1,294 ± 25	-11.9	12.8	Fish bone, spine
BN-L-3	LIA 2	BAF	[2626] <1378>	BRAMS-1729.1.1	0.8230 ± 0.0026	1,565 ± 26	-	-	Limpet
BN-L-4	LIA 2	BAF	[2626] <1378>	BRAMS-1730.1.1	0.8211 ± 0.0026	1,584 ± 26	-	-	Limpet
BN-F-1	LIA 2	BAG	[1075]	BRAMS-1717.1.1	0.8288 ± 0.0026	1,509 ± 25	-11.4	14.9	Fish bone, mandibula?
BN-L-7	EN	BBA	[1909] <10722>	BRAMS-1733.1.1	0.8172 ± 0.0026	1,622 ± 26	-	-	Limpet
BN-F-11	MN	BCC	[2707] <12070>	BRAMS-2049.1.1	0.8499 ± 0.0027	1,306 ± 25	-	-	Fish bone
BN-F-12	MN	BCC	[1008] <9549>	BRAMS-2050.1.1	0.8486 ± 0.0027	1,318 ± 25	-	-	Fish bone
BN-F-13	MN	BCC	[1008]	BRAMS-2051.1.1	0.8482 ± 0.0027	1,323 ± 25	-	-	Fish bone
BN-F-14	MN	BCC	[2656]	BRAMS-2052.1.1	0.8437 ± 0.0026	1,365 ± 25	-	-	Fish bone
BN-F-15	MN	BCC	[2653] <11498>	BRAMS-2053.1.1	0.8497 ± 0.0027	1,308 ± 25	-	-	Fish bone
BN-L-8*	MN	BCC	[1260] <9468>	BRAMS-2041.1.1	0.8421 ± 0.0026	1,380 ± 24	-	-	Limpet
BN-L-9	MN	BCC	[1008] <9451>	BRAMS-2042.1.1	0.8545 ± 0.0026	1,263 ± 25	-	-	Limpet
				BRAMS-2042.2.1	0.8574 ± 0.0026	1,236 ± 24			Duplicate BN-L-9
BN-L-10*	MN	BCC	[2653] <11493>	BRAMS-2043.1.1	0.8219 ± 0.0025	1,575 ± 24	-	-	Limpet
BN-L-11*	MN	BCC	[2653] <11493>	BRAMS-2044.1.1	0.8201 ± 0.0025	1,593 ± 25	-	-	Limpet
BN-W-1	MN	BCC	[2653] <114595>	BRAMS-2045.1.1	0.8551 ± 0.0026	1,257 ± 24	-	-	Winkle
BN-W-2*	MN	BCC	[2653] <114595>	BRAMS-2046.1.1	0.8180 ± 0.0025	1,614 ± 25	-	-	Winkle
BN-W-3*	MN	BCC	[2707] <12072>	BRAMS-2047.1.1	0.8566 ± 0.0026	1,243 ± 24	-	-	Winkle
BN-W-4	MN	BCC	[2707] <12072>	BRAMS-2048.1.1	0.8181 ± 0.0025	1,613 ± 25	-	-	Winkle
BN-F-4*	MN	AD	[69]	BRAMS-1720.1.1	0.8648 ± 0.0027	1,167 ± 25	-11.3	14.9	Fish bone, mandibula
BN-F-5	MN	AD	[69]	BRAMS-1721.1.1	0.8547 ± 0.0026	1,261 ± 25	-11.5	13.9	Fish bone, mandibula
BN-F-6	MN	AD	[69]	BRAMS-1722.1.1	0.8551 ± 0.0026	1,257 ± 25	-10.5	13.2	Fish bone, mandibula
BN-F-7*	LN	AG	[58]	BRAMS-1723.1.1	0.8540 ± 0.0026	1,268 ± 25	-11.4	14.1	Fish bone, mandibula
				BRAMS-1723.1.2	0.8573 ± 0.0026	1,237 ± 25			Duplicate BN-F-7
BN-F-8*	LN	AG	[58]	BRAMS-1724.1.1	0.8631 ± 0.0027	1,183 ± 25	-11.3	13.6	Fish bone, mandibula

Figure 7-8: Fish bones and shell ^{14}C dates (presented in the same order as Table 6-2) for layer BCC. The crosses correspond to the fish bones forming the group (c), the black dots correspond to the limpet and winkles forming group (a), the white dots limpets and winkles forming the Group (b) and the triangle the outlier limpet which could not fir in group (a) or (b).

Layer AD was dated from 3 fish bones, of these, two showed consistent results (combined to 1259 ± 18 BP; T' = 0.0, T'(5 %) = 3.8, υ = 1) whereas the other was of a younger date (BN-F-4: 1167 ± 18 BP), possibly relating to the mobility of fish (Russell *et al.* 2011).

Two fish bones dated from the LN period (Layer AG) gave results which were not statistically identical (T' = 5.0, T'(5 %) = 3.8, υ = 1).

7.4.2 Determination of the local variation in the MRE at Bornais

The local reservoir effect was calculated (Section 2.5.3.6) for every pair of terrestrial/marine organism per context (excluding the measurements previously suggested as being outliers). These were subjected to the χ^2 test at the 5 % level (per context and all together) before being averaged to obtain an estimate of the local ΔR (Table 7-3; both 1 and 2σ intervals are given but only the first one is used for discussion). No ΔR was calculated for contexts BBA and BBD which were dated only by one marine or terrestrial sample. And none for layer AD as the

measurements on the fish bones failed the χ^2 test. In the case of layer BCC three distinct MREs were calculated based on the 3 different groupings of marine species.

The ΔR value for context BAC (from LIA 2) was calculated from four terrestrial and four aquatic organisms to be -47 ± 23 (T' = 2.4, T'(5 %) = 19.7, υ = 11) for LIA 2 phase, from one terrestrial organism and two limpets (fish samples were excluded) for context BAF to be -165 ± 26 (T' = 0.2, T'(5 %) = 3.8, υ = 1), and from two terrestrial and one marine organism for context BAG to be -214 ± 26 (T' = 0.0, T'(5 %) = 3.8, υ = 1).

Table 7-3: Calculation of the ΔR values (1σ and 2σ intervals) for the different contexts.

Phase	Layer	ΔR (1σ)	ΔR (2σ)
LIA 2	BAC	-47 ± 23	-39 ± 26
	BAF	-165 ± 26	-163 ± 48
	BAG	-214 ± 26	-203 ± 55
MN	BCC - group (a)	-102 ± 35	-80 ± 33
	BCC - group (b)	248 ± 37	269 ± 35
	BCC - group (c)	-26 ± 40	-5 ± 37
	BCC - all	35 ± 150	56 ± 150
	AD	-84 ± 34	-74 ± 60

Concerning the BCC layer, the mean ΔR is 35 ± 150, which included a wide variability due to the significant differences, previously highlighted, for the three groups of marine organisms. The two terrestrial organisms highlighted as outlier were excluded. Individually, Group (a) gave a ΔR of -102 ± 35 (T' = 8.3, T'(5 %) = 23.7, υ = 14), Group (b) 248 ± 37 (T' = 12.3, T'(5 %) = 30.1, υ = 19) and Group (c) -26 ± 40 (T' = 17.5, T'(5 %) = 36.4, υ = 24). MREs if Groups (a) and (c) are identical within error and the difference in ^{14}C could be explained by the mobility of fish species (Russell *et al.* 2011), whereas Group (b) clearly shows a different local reservoir effect, which could be explained if shells were collected from two different areas at the site or if some older material was reused in this context.

The ΔR for layer AD was calculated to be -84 ± 34 level (T' = 0.0, T'(5 %) = 3.8, υ = 1), using only one terrestrial and two marine organisms. Apart from the layer BCC Group (b) all the

layers showed a negative ΔR varying from -214 ± 26 to -26 ± 40. This variation might reflect the low number of individuals used in 3 of the layers.

Overall, if Group (b) of the BCC layer is excluded due to its elevated value, the weighted average of all reservoir effect calculated per context is -115 ± 72, although this does not pass the χ^2 test at the 5 % level (T' = 32.9, T'(5 %) = 11.1, υ = 5). If we consider the 58 ΔRs calculated for every paired organisms these failed the χ^2 test (T' = 115.4, T'(5 %) = 75.6, υ = 57). If the pairs from layer BAG, which was only dated by one fishbone, and therefore may not be representative of the context, are excluded, and the pairs BN-F-14/SUERC-2684, BN-F-14/OxA1542 which showed highest ΔR values, the data are statistically identical (T' = 69.3, T'(5 %) = 71.0, υ =53) and ΔR averages to -65 ± 46. These data suggest there is no significant difference in the reservoir effect from the LIA to Norse period at the site.

7.4.3 Discussion and conclusions

Commonly a ΔR of 0 is taken for the British Isles assuming an MRE of 405 ± 10 (ΔR = 5 ± 40 or 19 ± 14), calculated for late 19th/early 20th century UK water (Harkness 1983; Reimer *et al.* 2002). More recent studies pointed out that this value is not valid for all time periods and locations (e.g. Reimer *et al.* 2002; Ascough *et al.* 2004). Reimer *et al.* (2002) calculated a ΔR of -33 ± 93 (varying from -208 to +207) for 14 archaeological sites from the west coast of Ireland, Scotland and the Orkney Isles with no visible time dependency over a 4,000-year range. More recently, Ascough *et al.* (2004, 2006, 2007a, 2007b, 2009, 2017) focussed on calculating ΔR from more sites using paired organisms from the North Atlantic for various time periods, whereas Russell *et al.* (2015) suggested using an offset value of -47 ± 52 for the period 3,500 BC - 1,450 AD in Scotland. The ΔR values from the Hebridean Islands (available in the literature) are summarised in Table 7-4. The overall results of such studies suggest that

an elevated ΔR (64 ± 93) during the Mesolithic was replaced by a lower range from the Neolithic to Medieval Ages (-126 ± 39 and -130 ± 36; Ascough *et al.* 2017). The weighted average of ΔR was calculated for the Bornais settlement is -65 ± 46, which is consistent with the data available in the literature for the West coast area of Scotland at the date of occupation of the settlement associated with Mound 2 (ca. 660 – 1400 AD).

Table 7-4: Summary of ΔR values published for the Hebridean Islands (sites location given in Appendix 8.4).

Location	Site	ΔR ± 1σ	Time period	Reference
Outer Hebrides Lewis and Harris	Guinnerso	-130 ± 36	1,460 - 1,630 AD	Ascough *et al.* 2017
	Bostadh	-56 ± 14	893 - 984 AD	Ascough *et al.* 2009
	Garenin	-85 ± 17	887 - 995 AD	Ascough *et al.* 2009
	Traigh na Beirigh	-126 ± 39	4,540 - 4,240 BC	Ascough *et al.* 2017
	Northton	64 ± 41	6,390 - 6,290 BC	Ascough *et al.* 2017
		79 ± 32	6,390 - 6,230 BC	Ascough *et al.* 2007a
Outer Hebrides North Uist	Baleshare	-79 ± 17	252 BC - 149 AD	Ascough *et al.* 2004
		68 ± 95	77 BC - 111 AD	Reimer *et al.* 2002
Outer Hebrides South Uist	Hornish point	-79 ± 17	252 BC - 149 AD	Ascough *et al.* 2004
		-184 ± 122 -146 ± 71	394 BC - 24 AD	Reimer *et al.* 2002
Inner Hebrides (& Mainland)	Carding Mill Bay	150 ± 28	3,641 - 3,521 BC	Russell *et al.* 2015
		86 ± 67	3,942 - 3,653 BC	Reimer *et al.* 2002
		-44 ± 91	3,965 – 3,714 BC	Reimer *et al.* 2002
	Sand	64 ± 41	6,480 - 6,420 BC	Ascough *et al.* 2017
		64 ± 19	6,480 - 6,420 BC	Ascough *et al.* 2007a

If layer BCC is considered, the MRE can be divided into 3 groups. In Group (c) the reservoir effect could reflect the mobility of the fish species, which may obtain their carbon through their diets from a variety of places or due to their trophic behaviours, which are affected by different MREs. The results from Groups (a) and (b) may correspond to two different collection points of the mollusc shells. Collection point (a) is likely to be located on the West Coast, particularly on the rocky promontory (Rubha Ardvule) ~ 2 km from the settlement (Figure 7-9a) due to its agreement with the ΔR values for other contexts at the site and previously reported literature values for this coastline. Group (b) could correspond to another collection point on the other side of the island. Bornais is located ~ 9 km from the East coast and ~ 4 km to the sea loch Eynort, therefore, one of these could correspond to a second collection point comprising a rocky area which would be a favourable habitat for molluscs.

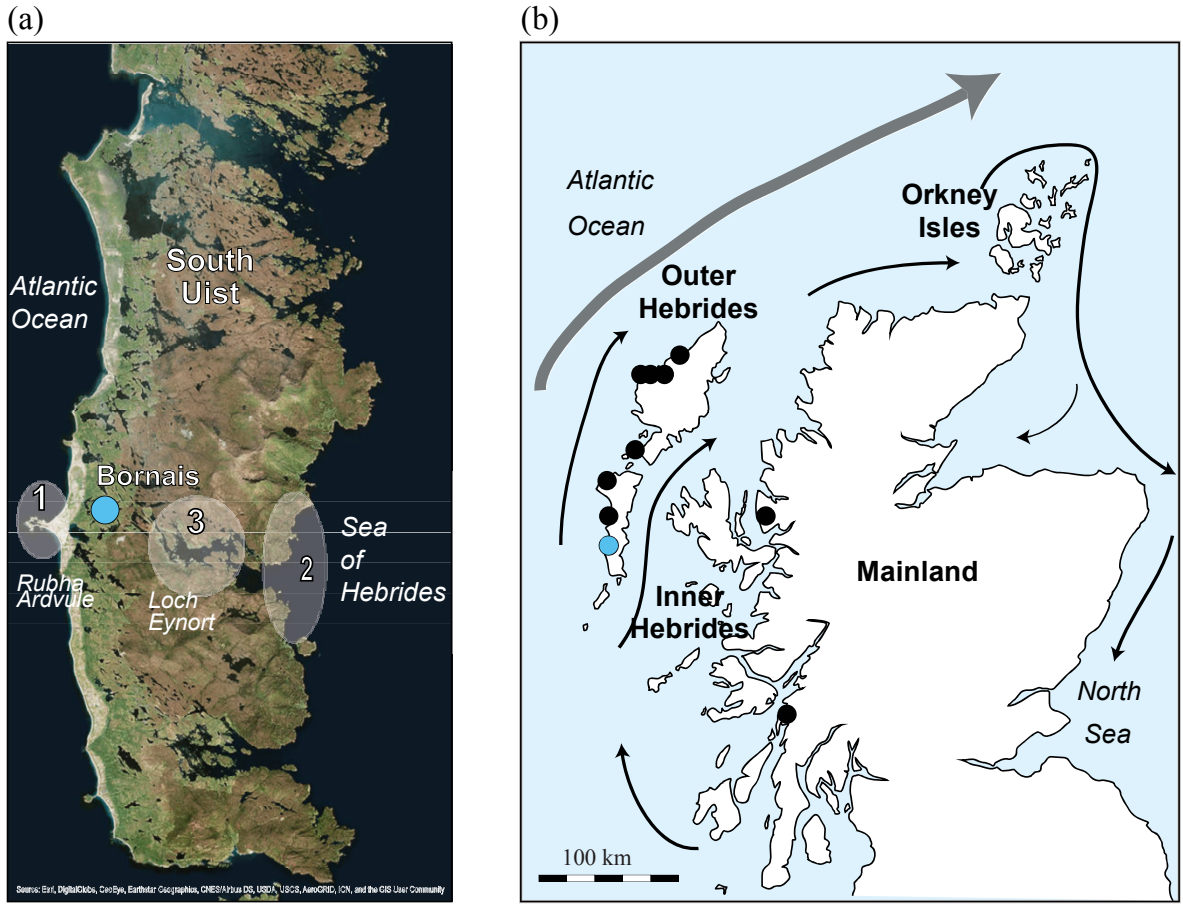

Figure 7-9: (a) Map of the South Uist isle showing the site of Bornais. Possible shell collection areas (1) on the West coast, (2) on East coast and (3) at the sea loch. (b) UK coastal currents with grey arrows corresponding to the Atlantic currents and black arrows to the coastal currents (adapted from Russell *et al.* 2015). Black dots correspond to the location of sites with reported ΔR values in Table 7-4 and blue dot shows the site of Bornais.

Earlier studies (Ascough *et al.* 2009; Russell *et al.* 2015) presented a map showing two different coastal currents around the Hebrides Isles, which could result in a variation in ΔR on the two coasts of the island (Figure 7-9b; Appendix 10.4). The MRE for the Inner Hebrides and Outer Hebrides were the same during the early Holocene but was higher in the Inner Hebrides during the late Holocene, suggesting a different MRE existed at the East coast at certain time periods (Ascough *et al.* 2007b, 2017). The ΔR values reported previously are, however, not as high as the 248 ± 37 calculated herein for the group of shells corresponding to Group (b), but these were from a different time period to those previously reported. This elevated ΔR is above the normal 'noise' in MRE suggests that it does not correspond to an MRE issued of diverse coastal currents.

A second hypothesis would be that the shells came from the sea loch, which has a sheltered topography and limited opening to the sea (Figure 7-9a). Examples of such unmixed waters in sheltered topographies are available for fjordic waters in Denmark, which exhibited older ages than those for coastal areas (Heier-Nielsen *et al.* 1995) and waters from sea loch in mainland Scotland exhibited slightly younger ages probably due to the high freshwater input (Cage *et al.* 2006). The sea loch Eynort is surrounded by small freshwater lochs surrounded by peat vegetation (Bennett *et al.* 1990), which could be the source of the runoff of 'old' C to the sea loch leading to higher MREs values calculated for Group (b). Therefore this value would a FRO (Alves *et al.* 2018). These data reflect the difficulty in determining the correspond of a mixing of MRE and FRO thus the ΔR calculated cannot be considered as an MRE if it includes behaviour of past populations and their diets including the locations for gathering molluscs species.

The last hypothesis to explain such a result would be that some older shells got introduced in a more modern context. Thanks to their robust nature, shells can be moved without obvious damage. Thus, it is not possible to distinguish fresh shells from residual ones. Shells could be recovered in a more modern context by disruption of the layers. However, no archaeological evidence of layer disruption supports this hypothesis. It is also possible that older shells were brought in the house for another purpose than consumption (e.g. decoration). Such past behaviour would be difficult to identify as this would not be visible by archaeological evidence.

7. 5 Radiocarbon dates on pottery vessels.

7.5.1 Radiocarbon dates on pottery vessels at Bornais

7.5.1.1 CSRA dates

TLEs from 22 sherds and seven visible residues were dated. Furthermore, dates on six of those potsherds were duplicated to test the spatial homogeneity in the mixing of marine/terrestrial lipid residues in a potsherd (Table 7-5). A total of 18 radiocarbon determinations of pottery vessel $C_{16:0}$ and $C_{18:0}$ FAs successfully passed in the internal quality control criterion, three failed and seven only generated one target. These seven were not considered further as it was impossible to evaluate their accuracy.

Of the six pottery vessels replicated two failed the internal criterion the first analysis but the second dating for potsherd BN-35 successfully passed the internal quality control criterion, whereas BN-101 only yielded sufficient material to generate the $C_{16:0}$ target. Of the remaining sherds, three demonstrated that replicate extractions yielded statistically indistinguishable results. The duplicate analysis on potsherd BN-74 produced statistically non-identical results. Both extractions, however, successfully passed the internal quality control criterion and, as previously discussed, it is unlikely that both isolated FAs could be contaminated to the same degree (giving rise to identical, but incorrect, dates). If the potsherd is well dated both time this difference could reflect an inhomogeneous partitioning of the marine and terrestrial products in the same potsherd.

Table 7-5: FAs radiocarbon dates on pottery vessels from the site of Bornais. VR corresponds to the visible residues.

Sample	Phase	Layer	BRAMS #	mCO_2 (µg)	$F^{14}C \pm 1\sigma$	Age ± 1σ (BP)	σ range	Comments
BN89-$C_{16:0}$	LIA 2	BAC	1549.1.1	199	0.8404 ± 0.0029	1396 ± 29	••	No aquatic biomarkers
BN89-$C_{18:0}$	LIA 2	BAC	1549.1.2	312	0.8468 ± 0.0030	1336 ± 27		
BN89-$C_{16:0}$	LIA 2	BAC	1549.2.1	230	0.8396 ± 0.0029	1404 ± 30	••	
BN89-$C_{18:0}$	LIA 2	BAC	1549.2.2	373	0.8482 ± 0.0030	1322 ± 29		
BN74-$C_{16:0}$	LIA 2	BAC	1551.1.1	388	0.8487 ± 0.0027	1394 ± 27	••	APAAs
BN74-$C_{18:0}$	LIA 2	BAC	1551.1.2	534	0.8433 ± 0.0026	1369 ± 26		
BN74-$C_{16:0}$	LIA 2	BAC	1551.2.1	379	0.8507 ± 0.0030	1299 ± 29	•	
BN74-$C_{18:0}$	LIA 2	BAC	1551.2.2	448	0.8535 ± 0.0030	1273 ± 29		
BN77-$C_{16:0}$	LIA 2	BAF	1605.1.1	234	0.8439 ± 0.0028	1364 ± 29	•	No aquatic biomarkers
BN77-$C_{18:0}$	LIA 2	BAF	1605.1.2	293	0.8426 ± 0.0028	1375 ± 28		
BN87-$C_{16:0}$	LIA 2	BAF	1604.1.1	175	0.8515 ± 0.0029	1292 ± 29	•	APAAs
BN87-$C_{18:0}$	LIA 2	BAF	1604.1.2	246	0.8490 ± 0.0028	1315 ± 28		
BN88-$C_{16:0}$	LIA 2	BAG	1548.1.1	216	0.8073 ± 0.0030	1720 ± 28	•	APAAs, DHYAs
BN88-$C_{18:0}$	LIA 2	BAG	1548.1.2	141	0.8063 ± 0.0029	1729 ± 30		
BN88-$C_{16:0}$	LIA 2	BAG	1548.2.1	228	0.8066 ± 0.0030	1726 ± 30	•	
BN88-$C_{18:0}$	LIA 2	BAG	1548.2.2	165	0.8065 ± 0.0030	1728 ± 32		
BN35-$C_{16:0}$	EN	BBD	1552.1.1	112	0.8412 ± 0.0033	1389 ± 33	X	APAAs, DHYAs
BN35-$C_{18:0}$	EN	BBD	1552.1.2	142	0.8553 ± 0.0030	1255 ± 30		
BN35-$C_{16:0}$	EN	BBD	1552.2.1	136	0.8665 ± 0.0034	1151 ± 33	•	
BN35-$C_{18:0}$	EN	BBD	1552.2.2	125	0.8654 ± 0.0035	1161 ± 34		
BN91-$C_{16:0}$	EN	BBD	1603.1.1	207	0.8429 ± 0.0028	1372 ± 29	-	APAAs, DHYAs - No internal control
BN91-$C_{18:0}$	EN	BBD	1603.1.2	*79*	-	-		
BN101-$C_{16:0}$	EN	BBD	1550.1.1	110	0.8793 ± 0.0032	1033 ± 27	X	No aquatic biomarkers
BN101-$C_{18:0}$	EN	BBD	1550.1.2	105	0.8380 ± 0.0033	1420 ± 31		
BN101-$C_{16:0}$	EN	BBD	1550.2.1	110	0.8329 ± 0.0032	1469 ± 33	-	No aquatic biomarkers - No internal control
BN101-$C_{18:0}$	EN	BBD	1550.2.2	*70*	-	-		
BN105-$C_{16:0}$	EN	BBD	1547.1.1	164	0.8519 ± 0.0030	1288 ± 30	•	No aquatic biomarkers
BN105-$C_{18:0}$	EN	BBD	1547.1.2	128	0.8562 ± 0.0031	1247 ± 31		
BN105-$C_{16:0}$	EN	BBD	1547.2.1	120	0.8432 ± 0.0033	1370 ± 34	••	
BN105-$C_{18:0}$	EN	BBD	1547.2.2	117	0.8527 ± 0.0034	1280 ± 34		
BN110-$C_{16:0}$	EN	BBA	1608.1.1	184	0.8443 ± 0.0028	1360 ± 29	••	APAAs
BN110-$C_{18:0}$	EN	BBA	1608.1.2	153	0.8519 ± 0.0030	1288 ± 30		
BN115-$C_{16:0}$	MN	BCA	1609.1.1	219	0.8842 ± 0.0029	989 ± 28	•	No aquatic biomarkers
BN115-$C_{18:0}$	MN	BCA	1609.1.2	214	0.8847 ± 0.0030	984 ± 29		
BN139-VR	MN	BCC	1975.1.1	171	0.8415 ± 0.0029	1386 ± 28	-	Visible residue - No aquatic biomarkers
BN142-$C_{16:0}C_{18:0}$	MN	BCC	2069.1.1	238	0.8822 ± 0.0030	1007 ± 29	-	DHYAs - No internal control

BN149-$C_{16:0}C_{18:0}$	MN	BCC	2064.1.1	145	0.8025 ± 0.0032	1768 ± 34	-	DHYAs - No internal control
BN149-VR	MN	BCC	1976.1.1	706	0.8778 ± 0.0027	1047 ± 25	-	Visible residue - APAAs, DHYAs, TMTD -
BN160-$C_{16:0}$	MN	BCC	2066.1.1	-	0.8580 ± 0.0029	1230 ± 29	•	No aquatic biomarkers
BN160-$C_{18:0}$	MN	BCC	2066.1.2	216	0.8650 ± 0.0031	1165 ± 31		
BN160-VR	MN	BCC	1977.1.1	734	0.8891 ± 0.0028	945 ± 25	•	Visible residue - No aquatic biomarkers
BN160-VR	MN	BCC	1977.1.1	822	0.8918 ± 0.0028	920 ± 25		
BN165-$C_{16:0}$	MN	BCC	2063.1.1	311	0.8741 ± 0.0030	1080 ± 29	•	No aquatic biomarkers
BN165-$C_{18:0}$	MN	BCC	2063.1.2	285	0.8785 ± 0.0030	1040 ± 29		
BN167-$C_{16:0}C_{18:0}$	MN	BCC	2068.1.1	225	0.8511 ± 0.0031	1295 ± 31	-	APAAs, TMTD - No internal control
BN167-VR	MN	BCC	1978.1.1	982	0.8659 ± 0.0027	1157 ± 25	-	Visible residue, no aquatic biomarkers
BN168-$C_{16:0}$	MN	BCC	2061.1.1	123	0.8601 ± 0.0035	1211 ± 34	X	No aquatic biomarkers
BN168-$C_{18:0}$	MN	BCC	2061.1.2	253	0.8762 ± 0.0035	1062 ± 34		
BN173-$C_{16:0}C_{18:0}$	MN	BCC	2067.1.1	167	0.8575 ± 0.0032	1234 ± 32	-	APAAs, DHYAs, TMTD - No internal control
BN174-$C_{16:0}$	MN	BCC	2062.1.1	219	0.8664 ± 0.0031	1152 ± 31	••	APAAs
BN174-$C_{18:0}$	MN	BCC	2062.1.2	296	0.8758 ± 0.0034	1065 ± 33		
BN174-VR	MN	BCC	1979.1.1	906	0.8891 ± 0.0028	944 ± 25	-	Visible residue – APAAs, TMTD
BN176-VR	MN	BCC	1980.1.1	698	0.8919 ± 0.0028	919 ± 25	-	Visible residue – APAAs, TMTD
BN38-$C_{16:0}$	MN	AD	1606.1.1	121	0.8972 ± 0.0032	871 ± 31	-	No aquatic biomarkers - No internal control
BN36-$C_{16:0}$	LN	AG	1607.1.1	201	0.9090 ± 0.0030	767 ± 29	••	APAAs, DHYAs
BN36-$C_{18:0}$	LN	AG	1607.1.2	115	0.9034 ± 0.0034	816 ± 31		
BN131-$C_{16:0}$	LN	CDG	1653.1.1	*65*	*0.9090 ± 0.0038*	*1327 ± 38*	•	No aquatic biomarkers - Small sample size excluded

• $C_{16:0}$ and $C_{18:0}$ dates identical within 1σ
•• $C_{16:0}$ and $C_{18:0}$ dates identical within 2σ
X $c_{16:0}$ and $C_{18:0}$ dates non-identical within 2σ

The dates on visible and adsorbed lipids from two potsherds (which passed the internal quality control) were non-identical on a statistical basis, with the visible residues being younger to 268 years for potsherd BN-160 and 171 years for potsherd BN-174. This result was surprising especially in the case of BN-160 considering the visible and invisible residues produced similar results by ORA and $\delta^{13}C$ values suggesting similar results for ^{14}C analyses as well (Appendix 8.2). This emphasises the fact that the dates from the two different lipid sources in the same vessel do not necessarily relate to the same cooking event (i.e. the absorbed lipids integrate a number of cooking events while the visible residues correspond to a single cooking event), as was seen in the dating of visible and absorbed residues at Cliffs End Farm (Chapter 4).

7.5.1.2 Comparison with available dates

The four sherds from the BAC and BAF contexts of phase LIA2 were shown to have similar $\delta^{13}C$ values and radiocarbon ages ranging between the age of the terrestrial organisms and their marine analogues (BN-74: 1,383 ± 23 BP (1st extraction) or 1,286 ± 25 BP (2nd extraction); BN-77: 1,370 ± 24 BP; BN-88: 1,725 ± 15 BP and BN-89: 1,365 ± 25 BP). This was also the case for the two sherds (BN-74 and BN-77) which did not exhibit aquatic biomarkers. These dates suggest, therefore, some mixing between terrestrial and marine resources in all the sherds. The sherd BN-88 from the BAG context exhibited not only the most enriched $\delta^{13}C$ values but also the oldest age obtained in this investigation. This date is older than the marine reference fish bone from this context, which was excluded from the overall ΔR calculation, or, indeed the reference fish bones from LIA 2 phases. The second dating of the potsherd confirmed the accuracy of the compound-specific ^{14}C measurement, suggesting that this older age is not explainable by contamination occurring during sample preparation. Thus, these lipid residues could be derived from a pure marine fat/oil residue from shellfish (not dated this context) rather

than fish. The potsherd could also be residual from the LIA 1 phase, however, no aquatic biomarkers were detectable in TLEs for this phase (Cramp forthcoming).

For the EN phase, the three pots (BN-35: 1,156 ± 27 BP; BN-105: 1,261 ± 17 BP; BN-110: 1,326 ± 25 BP) showed intermediate ages between the terrestrial organisms and their marine analogues. This suggests, therefore, some mixing between terrestrial and marine resources in all the sherds for this phase, including BN-105, which did not exhibit aquatic biomarkers.

The three sherds from the BCC context of the MN phase (BN-160: 1,201 ± 25 BP; BN-165: 1,060 ± 25 BP and BN-174: 1,115 ± 26 BP) exhibit intermediate ages between the age of the terrestrial organisms and their marine analogues, including two sherds (BN-160 and BN-165) which also did not contain aquatic biomarkers. The radiocarbon dates, therefore, suggest the mixing of terrestrial and marine resources in all the vessels for this phase. The visible residue dates from this context (BN-160VR and BN-174VR) are compatible with the terrestrial organism (T' = 7.7, T'(5 %) = 12.6, υ = 6; excluding outliers highlighted Section 7.4.1.1) suggesting no visible MRE for such residues. The potsherd BN-115 (987 ± 24 BP, context BCA not dated), which did not contain aquatic biomarkers exhibited an age consistent with the MN phase (T' = 8.1, T'(5 %) = 11.1, υ = 5). The $\delta^{13}C$ values lie outside the reference ellipses of ruminant animals possibly due to the contribution of pig rather than marine products to this vessel or an inland effect (Cramp and Evershed 2014).

For the LN phase, the FA date on the pot BN-36 (786 ± 25 BP) is younger than that of the terrestrial organisms (BN-MB-7: 930 ± 25 BP). Based on the $\delta^{13}C$ values, the sherd plots close to the reference dairy fat ellipses despite containing aquatic biomarkers. This result is surprising and suggests that the biomarkers demonstrate the processing of marine products in a small enough quantity that would not affect a radiocarbon date. The potsherd could also be

an intrusive material from a younger phase, or, the dating of this phase, based on only one terrestrial organism is erroneous. Younger ages from other LN contexts were obtained in a range of 900 to 650 BP (uncalibrated), which could support this latter hypothesis (Marshall *et al.* forthcoming). The sherd could also be intrusive in the context it was recovered, or the ^{14}C age is not accurate.

7.5.1.3 Discussion

Here, one of the important issues to be addressed was whether the internal quality control criterion on the two FAs would remain valid when dating mixed marine/terrestrial products. A total of 17 pairs of measurements on individual FAs (out of 19) passed the internal quality control criterion. This suggests that the different proportion of $C_{16:0}$ and $C_{18:0}$ FAs in the two classes of animal products do not significantly affect the internal quality control. The duplicate on pot BN-74 highlights the fact that the mixing of marine/terrestrial products in a pottery vessel might not necessarily lead to homogenous deposition and lead to significantly different ages. In addition, there can be a significant discrepancy in the radiocarbon dates from visible and invisible residues due to them representing different processing events, providing a further example of the phenomenon encountered with the dating of Cliff End Farm, where dates from adsorbed residues were significantly older than those of visible residues on the same potsherds.

Overall, the sherds which were dated presented intermediate ages between contemporaneous terrestrial organisms and their marine counterparts, including four sherds that did not show any aquatic biomarkers. Although characteristic marine biomarkers were not identified in the TLEs, the radiocarbon dates do suggest the processing of marine products in the vessel highlighting the fact that the absence of aquatic biomarkers is not necessarily synonymous with a lack of aquatic products processing, and therefore, no reservoir effect. Thus, CSRA on pottery vessels

could reveal the processing of marine products when biomarker analyses $\delta^{13}C$ analyse failed to do so. Only one sherd displayed aquatic biomarkers but no apparent MRE, but its recovery context is not well-dated. There seems to exist a correlation between increasing radiocarbon ages with enriched $\delta^{13}C$ values of the $C_{16:0}$ and $C_{18:0}$ FAs. This reflects the increasing abundance of marine products mixed with terrestrial animal products leading to lipid residues exhibiting heavier $\delta^{13}C$ values and larger influence from the MRE. In addition, the difference between the visible and adsorbed residues was once again reinforced.

7.5.2 Quantification of the mixing of marine and terrestrial fats/oils for the correction and calibration of ^{14}C dates on potsherd at Bornais

7.5.2.1 Methods for the quantification of marine/terrestrial products in residues

The mixing of marine/terrestrial organisms was quantified by two different methods using either ^{14}C dates or $\delta^{13}C$ values (summarised in Figure 7-10; Section 2.5.3.7). This approach was adopted based on the apparent correlation between enriched $\delta^{13}C$ and ^{14}C values. By comparing the mixing ratios obtained by the two methods it is possible to evaluate whether $\delta^{13}C$ values on the FAs can be used to estimate the proportion of marine oil/fats (cf. human bone collagen) as a means of correcting radiocarbon dates on pottery vessels for the MREs. This constitutes an important consideration especially for sites where terrestrial and marine remains are absent from the archaeological record. The percentage of aquatic derived resources calculated by ^{14}C dates and $\delta^{13}C$ values using both the adipose and the milk end-members were then implemented in the OxCal software (Bronk Ramsey 2009), alongside the ΔR value determined earlier, for calibration of the mixed resources.

The first method of quantifying the percentage (with associated uncertainty) of marine fat/oil uses the weighted average of radiocarbon determinations on the terrestrial and marine

organisms, from the same contexts/phase of the potsherds dated, as end-members (Equation 2-17, Section 2.5.3.7). This method provides therefore, a reference value for the percentage of marine fat/oil present in the FAs ^{14}C dated.

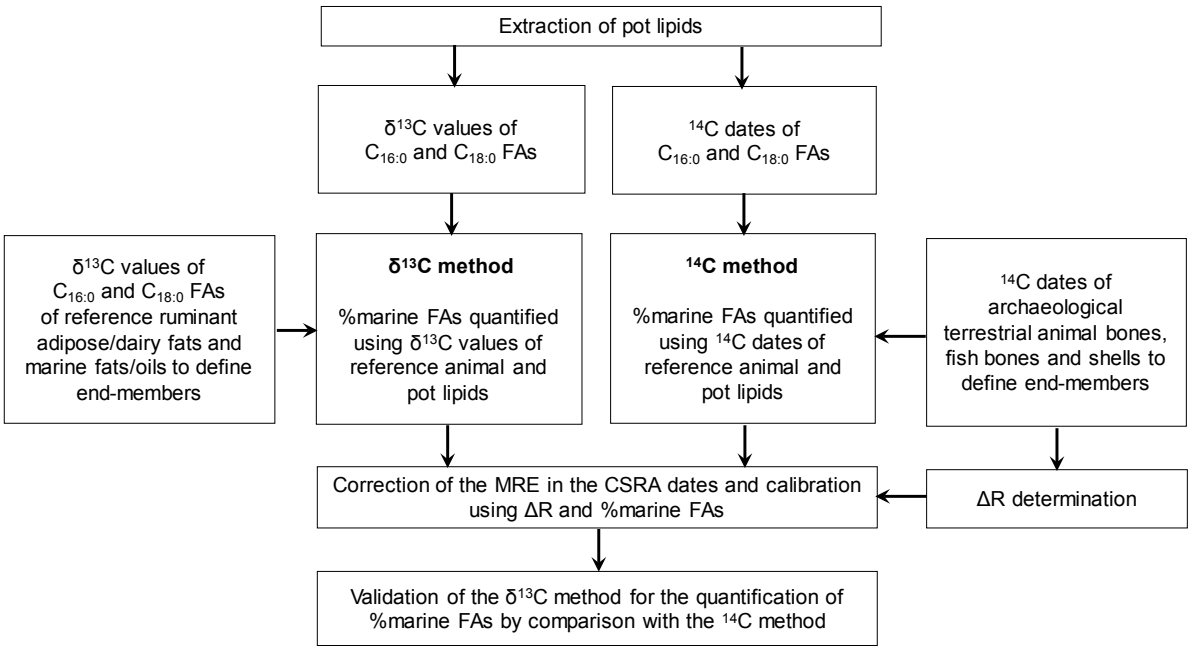

Figure 7-10: Flowchart showing the method used to evaluate the validity of the $\delta^{13}C$ values method for the estimation of the percentage of marine products and correction of the CSRA dates on the FAs.

The second method uses the $\delta^{13}C$ values (Section 2.5.3.7) of the UK reference animals from Copley *et al.* (2003) for cattle and sheep raised on a pure C_3 diet, as the terrestrial end-member (pigs were considered to not be processed in pots due to their relatively low abundance at the site (Sharples *et al.* 2016). The end-member corresponds to the average of individual palmitic and stearic acids, including their respective standard deviations (Equation 2-16), i.e. $\delta^{13}C_{16:0} = -30.0 \pm 0.6$ ‰ and $\delta^{13}C_{18:0} = -32.2 \pm 0.6$ ‰ for the adipose fats and $\delta^{13}C_{16:0} = -29.2 \pm 1.0$ ‰ and $\delta^{13}C_{18:0} = -34.0 \pm 0.9$ ‰ for dairy fats. Both ruminant adipose and dairy values were used as end-members to evaluate whether one should be used over the another.

Carbon isotope values from Cramp and Evershed (2014) for fish, winkles and limpets only (corrected for the Suess effect) captured from the UK waters, including the northern isles of

Scotland, were used as the marine end-member. The reference ellipse for marine organisms is broad (Cramp and Evershed 2014) and the use of standard deviation would underestimate the proportion of marine lipids. Therefore, the difference between the extreme values in the database (Min = -18.2 and -16.9 ‰ and Max = -28.1 and -26.8 ‰ for $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$, respectively) was used as the error bars in the marine end-members. The raw values were averaged for individual FAs giving $\delta^{13}C_{16:0}$ = -22.7 ± 9.2 ‰ and $\delta^{13}C_{18:0}$ = -21.7 ± 9.8 ‰ as marine end-members. The relationship between the relative proportions of marine and terrestrial fats and the $\delta^{13}C$ values is non-linear due to the differing relative abundances (percentage) of the of FAs in the end member foodstuffs (Mukherjee *et al.* 2005), however, based on the success of the internal quality control on the CSRA dates (which suggests a linear relationship within measurement errors) of the $C_{16:0}$ and $C_{18:0}$ FAs the intensities of FAs were not included in the mixing curve for the terrestrial and marine fats/oils (see Equation 2-17, Section 2.3.7). The percentages obtained on both FAs were then combined as a weighted average with error calculated as in Equation 2-16.

7.5.2.2 Quantification, correction and calibration of CSRA on FAs showing mixing of terrestrial and marine fats/oils

The mixing of marine/terrestrial organisms was only quantified for the sherds which passed the internal quality control criterion. The CSRA dates of lipids which showed a full marine (BN-88) or terrestrial age (BN-36) were not considered as quantification of the percentage of marine fat/oil is not required in these cases. Furthermore, potsherds from the layer BAF which yielded only one doubtful age on terrestrial organisms and the layer BCA which showed no date on terrestrial organism were excluded. The percentages of marine products present in the TLEs (n = 8) quantified using both $\delta^{13}C$ values and ^{14}C dates on FAs are shown in Table 7-6, then calibrated (Sections 2.5.3.7, 7.5.2.1).

Table 7-6: Percentage of aquatic resources in potsherds from Bornais calculated by radiocarbon determinations and stable isotopes analysis on individual fatty acids.

Phase	Context	Sherd	Mixture ^{14}C method		Mixture $\delta^{13}C$ method		
			$\%_{Aqua}$	Reservoir context used	$\%_{Aqua}$ (adipose)	$\%_{Aqua}$ (milk)	$\Delta^{13}C$ (‰)
LIA 2	BAC	BN89	26 ± 12	BAC	30 ± 36	37 ± 39	-2.8
		BN74	31 ± 12 4 ± 11	BAC (1 ext) BAC (2 ext)	30 ± 37	38 ± 39	-2.5
EN	BBD	BN35	23 ± 9	BBA/BBD	9 ± 43	23 ± 40	-6.0
		BN105	42 ± 10	BBA/BBD	6 ± 37	21 ± 33	-5.4
	BBA	BN110	51 ± 11	BBA/BBD	63 ± 60	66 ± 62	-0.5
MN	BCC	BN160	75 ± 16 38 ± 7 57 ± 12	BCC a +c BCC b BCC all	14 ± 35	26 ± 34	-4.6
		BN165	32 ± 14 16 ± 7 24 ± 10	BCC a +c BCC b BCC all	23 ± 36	33 ± 37	-3.7
		BN174	49 ± 15 25 ± 7 37 ± 11	BCC a +c BCC b BCC all	39 ± 44	46 ± 46	-2.6

7.5.2.2.1 LIA phase

For the LIA phase, the percentage of terrestrial and marine fats mixed in the pot BN-89 is 26 ± 12 % with ^{14}C dates, 30 ± 36 and 37 ± 39 % with $\delta^{13}C$ values using adipose and milk end-members, respectively. All these results are statistically identical even though their $\Delta^{13}C$ values > -3.1 ‰ suggest the use of ruminant carcass rather than dairy products. Concerning potsherd BN-74 the first extraction of lipid yielded 31 ± 12 % of marine fat/oil using ^{14}C dates and 30 ± 37 and 38 ± 39 % using $\delta^{13}C$ values on adipose and milk products as end-member, respectively. Once again, these results are statistically identical and no significant difference is visible for both adipose and milk FAs used as end-members. Concerning the 2nd lipid extraction of the pot BN-74 which yielded results statistically different to the 1^{rst} extraction (Section 7.5.1) showed a percentage of marine products of 4 ± 11 % using ^{14}C as end-members, suggesting an overestimation of the proportion of marine products in the pots based on the $\delta^{13}C$ values. As mentioned previously (Section 7.5.1.1) this potsherd is likely affected by a differential deposition of the marine fats in certain areas of the vessel explaining such difference.

The calibrated ^{14}C measurements for pots from the phase LIA 2 using ΔR -65 ± 45 are presented in Figure 7-11. The range of calibrated terrestrial dates for BN-MB3, BN-MB4 and BN-MB6 were respectively 672 - 773 AD, 662 - 769 AD and 685 - 772 AD (95% probability). The pot BN-89 was calibrated to 656 - 831 AD by radiocarbon estimates, to 654 – 960 AD by adipose end-member and to 656 - 974 AD by dairy end-member (95 % probability). The pot BN-74 (1st extraction only) was calibrated to 654 - 825 AD by radiocarbon estimates, to 650 - 950 AD by adipose end-member and to 651 - 962 AD by dairy end-member (95 % probability). In both cases, the $\delta^{13}C$ calculations showed a wider probability distribution than that obtained using radiocarbon dates likely due to the larger uncertainties associated with the proportion of marine-derived C. However, the calibrated range of the corrected CSRA measurements on pot lipids using both methods clearly overlap the calibrated range of the reference terrestrial organisms. There is no significant difference between the use of adipose or dairy $\delta^{13}C$ values as end-members.

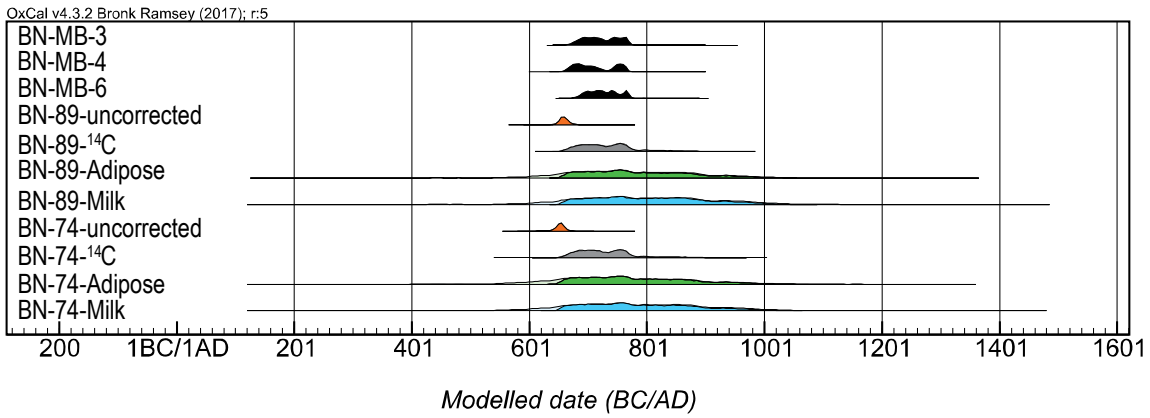

Figure 7-11: Probability distribution for an event to occur at a particular time for pots BN-89, and BN-74 after calibration correcting for the local reservoir effect and the percentage of marine products. The probability distribution plotted in black correspond to the age of terrestrial organisms (BN-MB-3, 4 and 6), in orange the uncorrected dates on potsherds, in grey the corrected date using the ^{14}C dates method for the quantification of the percentage of marine products, in green and blue the corrected dates using the $\delta^{13}C$ method using adipose and the milk, respectively, as end member (Table 7-6; OxCal v4.3,Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

7.5.2.2.2 EN phase

For the EN phase the unique marine organism from layer BBA and the two terrestrial organisms (not identical within error probably related to a long settlement) from layers BBD were used, thus the calculation using radiocarbon dates, in this instance, is not precise (Table 7-6). For the potsherds BN-35 and BN-105, $\Delta^{13}C$ values suggest the processing of dairy products, but the percentages of marine fat/oil calculated from the radiocarbon dates are statistically identical to the results obtained using both end-members. The same result was obtained for potsherd BN-110, where the $\delta^{13}C$ values suggests the mixing of aquatic and ruminant adipose products.

The calibrated ^{14}C measurements for pots from phase EN using a ΔR of -65 ± 46 are presented in Figure 7-12. The range of terrestrial dates for BN-MB8 and BN-MB10 were, respectively, 895 – 1,017 AD and 1,027 – 1,155 AD (95% probability). The date of pot BN-35 was calibrated to 858 – 1,175 AD using the adipose end-member and to 860 – 1,169 AD using the milk end-member (93 % probability). The use of $\delta^{13}C$ values for the quantification of marine products showed, in both cases, a calibrated range overlapping with the terrestrial organism BN-MB-8.

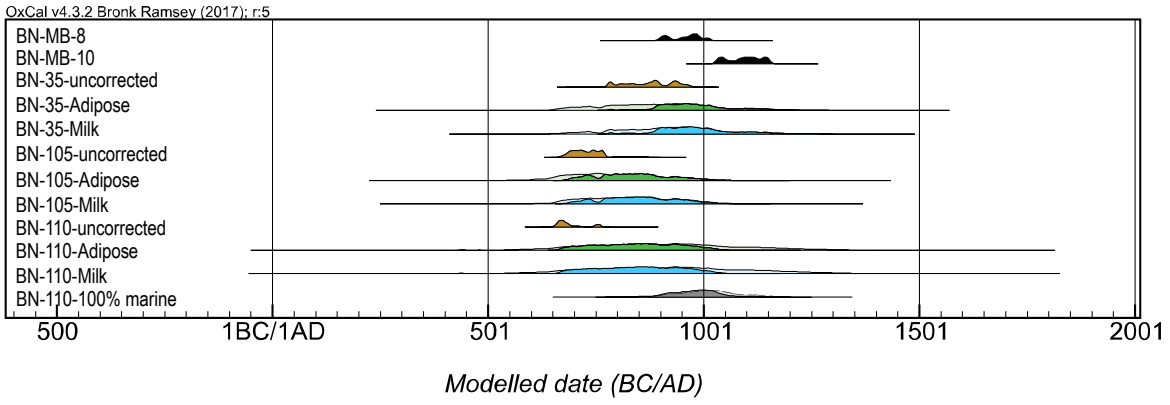

Figure 7-12: Probability distribution for an event to occur at a particular time for pots BN-35, BN-105 and BN-110 after calibration correcting for the local reservoir effect and the percentage of marine products. The probability distribution plotted in black correspond to the age of terrestrial organisms (BN-MB-8 and 10), in orange the uncorrected dates on potsherds, in green and blue the corrected dates using the $\delta^{13}C$ method using adipose and the milk, respectively, as end member (Table 7-6) and in grey the distribution corresponding to a theoretical estimates of 100 % marine (OxCal v4.3, Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

The pot BN-105 was calibrated to 686 - 995 AD using the adipose end-member and to 689 – 1,010 AD using the milk end-member (95 % probability). The end of the calibration correlates with the calibration range of the BN-MB8 but do not entirely overlap however, calibrated values of pottery vessels and terrestrial organisms would not necessarily overlap completely especially for long settlements. The pot BN-110 was calibrated to 674 -1,016 AD by adipose end-member and to 672 – 1,018 AD by milk end-member (95 % probability). Similarly, the end of the calibration corelates with the calibration range of the BN-MB8 but do not entirely overlap.

7.5.2.2.3 MN phase

For the MN phase context BCC, three estimates were obtained for the percentage of marine products using the ^{14}C method, based on the radiocarbon ages obtained from the Groups (a) and (c) combined by a weighted average (due to their agreement with the overall ΔR calculated Section 7.4.2), Group (b) of reference marine organisms, and an average MRE of those 3 groups. If the shells Group (b) are indeed intrusive, then the MRE in the pots is only affected by marine organisms of the Groups (a) and (c). If the shells Group (b) are contemporaneous, but from another point of location then, the potsherds could record an average MRE.

For all three pottery vessels the estimates of the proportion of marine fat/oil obtained using both adipose or milk as end-members, are statistically identical (within 1σ for BN-168 and BN-174 and within 2σ for BN-160) to those calculated using marine organisms. This could suggest that the pots dates record an average of all marine products processed (i.e. from a wide range of habitats) rather than from a specific point of collection. This hypothesis is supported by the marine organisms of the Group (a), (b) and (c) being recovered from the same contexts (and sub-layers). It should be noted that for potsherd BN-160 the percentage of marine products

calculated are 75 ± 15 and 38 ± 7 for Group (a) + (c) and Group (b) respectively against 14 ± 35 and 26 ± 34 % for adipose and milk as end-member respectively. The percentages of marine fat/oil quantified with the $\delta^{13}C$ values are not identical within a 1σ error (but is within a 2σ error) to the method using ^{14}C dates for MRE of Group (a) + (c) and the average but, are identical within a 1σ error of the Group (b). This could suggest that in this potsherd marine organisms from the Group (b) are more represented than those of Group (a) + (c), or that the potsherd is affected by a differential partitioning of marine fat/oil.

The ^{14}C measurements on pottery vessels from phase MN context BCC were calibrated using both the ΔR for the site (-65 ± 46) and also a weighted average ΔR (34 ± 32) of the three different reservoirs (Figure 7-13). The apparent age date from a pottery vessel is likely to be a representation of all three MREs rather than only a single one (as suggested by the mixtures calculated previously), if this hypothesis is valid. Therefore, a weighted average (i.e. even representation of the three MREs) is potentially a better estimate of the resulting MRE revealed in the pots than the 'true' ΔR (35 ± 150), which displays a very large uncertainty.

The range of calibrated terrestrial dates (excluding outliers) varies from 993 – 1,052 AD (55 % probability) and 1,081 – 1,152 AD (OxA-15522; 41% probability) to 1,039 – 1,206 AD (OxA-1540, 95 % probability).

With the use of ΔR = -66 ± 45 and percentage of marine calculated from Groups (a) + (c), the pot BN-165 was calibrated to 990 – 1,186 AD, by radiocarbon estimates, to 979 - 1,252 AD using the adipose end-member and to 984 – 1,262 AD using the milk end-member (95 % probability). The pot BN-174 was calibrated to 979 – 1,207 AD by radiocarbon estimates, to 896 – 1,244 AD using the adipose end-member and to 898 – 1,254 AD by the milk end-member

(95 % probability). Both potsherds showed calibrated ages in agreement with the terrestrial mammal bones dates.

With the use of ΔR = 34 ± 32 and percentage of marine calculated from all Groups, the pot BN-165 was calibrated to 990 – 1,172 AD, by radiocarbon estimates, to 980 - 1,291 AD using the adipose end-member and to 982 – 1,310 AD using the milk end-member (95 % probability). The pot BN-174 was calibrated to 984 – 1,189 AD by radiocarbon estimates, to 898 – 1,288 AD using the adipose end-member and to 900 – 1,298 AD by the milk end-member (95 % probability). Both potsherds showed calibrated ages in agreement with the terrestrial mammal bones dates. There is no significant difference in the calibration using the contribution from Groups (a) + (c) or all the Groups averaged.

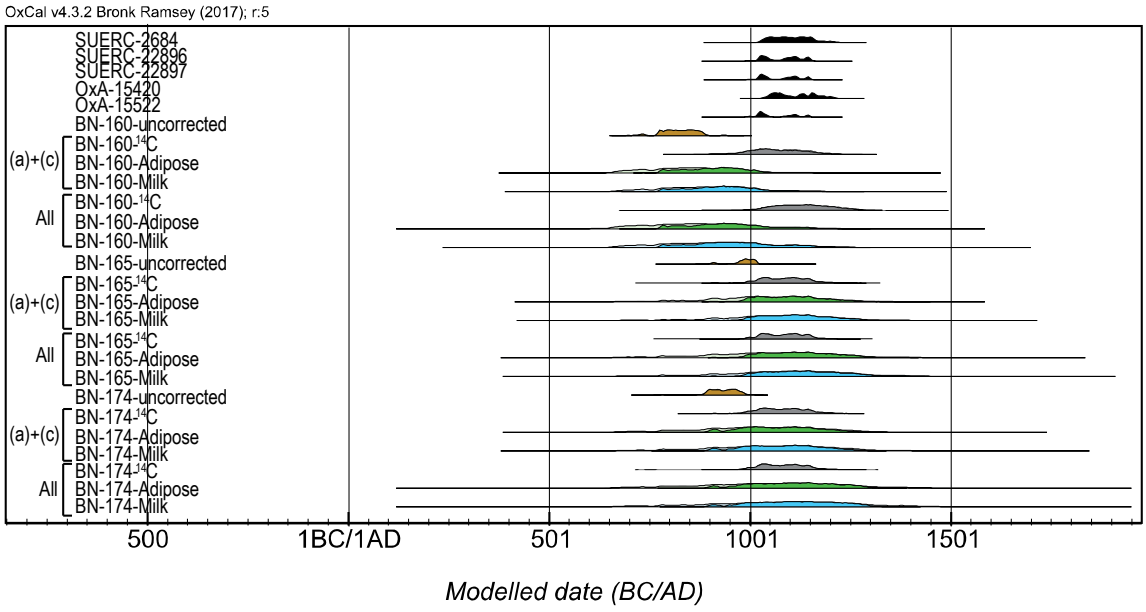

Figure 7-13: Probability distribution for an event to occur at a particular time for pots from the layer BCC after calibration correcting for the local MRE and the percentage of marine products. The probability distribution plotted in black correspond to the age of terrestrial organisms, in orange the uncorrected dates on potsherds, in grey the corrected date using the ^{14}C dates method for the quantification of the percentage of marine products, in green and blue the corrected dates using the $\delta^{13}C$ method using adipose and the milk, respectively, as end member (Table 7-6; OxCal v4.3, Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

With the use of ΔR = -65 ± 46 and percentage of marine calculated from Groups (a) + (c), the potsherd BN-160 was calibrated to 910 – 1,204 AD by radiocarbon estimates, to 770 - 1,110 AD by adipose end-member and to 772 – 1,123 AD by milk end-member (95 % probability) which corresponds to the beginning of the calibration of terrestrial organisms. With the use of ΔR = 34 ± 32 and percentage of marine calculated from all Groups, the potsherd BN-160 was calibrated to 1,015 – 1,266 AD by radiocarbon estimates, to 772 - 1,162 AD by adipose end-member and to 772 – 1,195 AD by milk end-member (95 % probability) which corresponds again to the beginning of the calibration of terrestrial organisms.

The calibrated date of this potsherd is different from the other two and could suggest a variable use of the marine organisms with a larger representation of the shells Group (b), if these are contemporaneous. As discussed in Section 7.4.2, this would nonetheless not correspond to an MRE and corrections as previously performed cannot be done in this case. However, if the hypothesis on of shells Group (b) being intrusive is valid, then a differential partitioning of marine/terrestrial lipid or residual potsherd could explain the results unless the CSRA date is inaccurate.

7.5.2.3 Limitations of using $\delta^{13}C$ values as end-members

The first limitation of the use of $\delta^{13}C$ values as end-members corresponds to an inhomogeneity of lipid deposition in the potsherd, as illustrated with potsherd BN-74 where two different extractions of the same potsherd yielded statistically distinguishable results. This issue could nonetheless, be overcome by measuring $\delta^{13}C$ values and ^{14}C dates on the same TLE.

The second limitation concerns the wide range of reference values (from ca. -26 ‰ to -20 ‰) of marine organisms. These reference ellipses commonly plotted comprise only 68 % of the reference values (i.e. 1-σ). The average values (for fish and gastropods only) used as end

member in this thesis are $\delta^{13}C_{16:0}$ = -22.7 ± 9.2 ‰ and $\delta^{13}C_{18:0}$ = -21.7 ± 9.8 ‰ and are not centred in the ellipses. Therefore, potsherds with $\delta^{13}C$ values plotting at the edge of the reference marine ellipse can be purely marine but, the percentage of marine fat/oil deposited in the sherd can be underestimated using the mixing curves (Figure 7-14; Sections 2.5.3.7, 7.5.2.1).

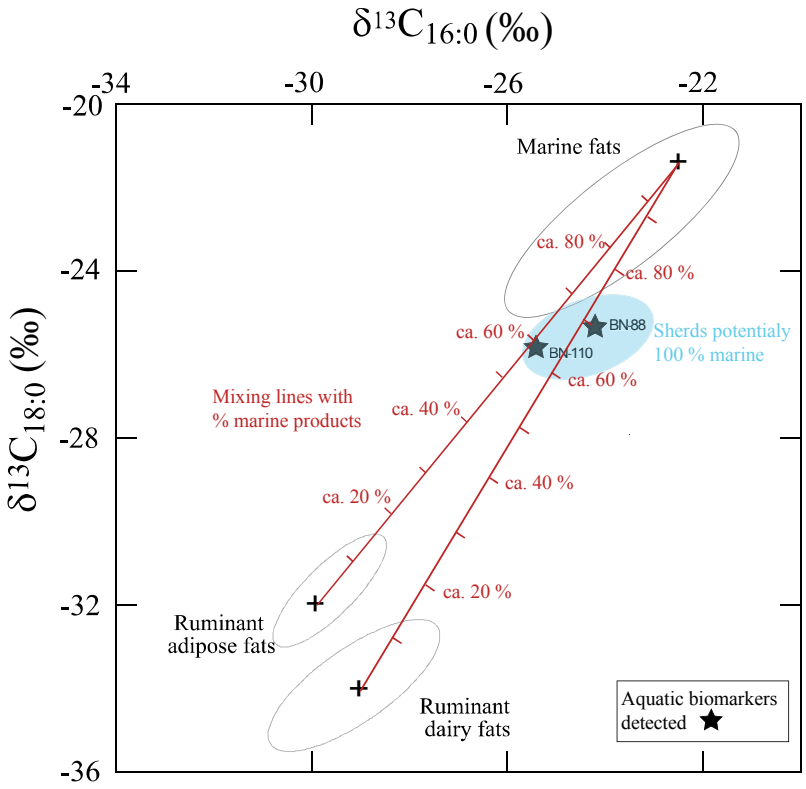

Figure 7-14: Scatter plot of $\delta^{13}C_{18:0}$ plotted against $\delta^{13}C_{16:0}$ showing the reference ellipses for UK ruminant and marine organisms and the theoretical mixing lines (Section 7.5.2.1) of the two commodities with the approximate percentage of marine fat/oil marked on the lines. Crosses correspond to the position of the averages used as end-member and the stars correspond to the values of potsherd BN-88 and BN-110.

To illustrate this, the percentage of marine fat/oil was quantified using $\delta^{13}C$ values for potsherd BN-88 which contains only marine fats based on the CSRA dates. This potsherd showed $\delta^{13}C_{16:0}$ = -24.2 ‰ and $\delta^{13}C_{18:0}$ = -25.4 ‰ which plots just outside the reference ellipse. The $\delta^{13}C$ method quantified a percentage of marine fat/oil of 69 ± 65 % and 71 ± 65 % with adipose and milk products used as end-member, respectively. The percentage of marine products is clearly underestimated in this case but with a wide uncertainty, suggesting that the large range

of reference values for UK organisms can bias the quantification of marine fat/oil especially when it is > 50 %. In such cases the uncertainty on the percentage of marine products would be over 50 %, which is not precise enough for an accurate calibration.

Another potsherd, BN-110 presented previously, with $\delta^{13}C_{16:0}$= -25.4 ‰ and $\delta^{13}C_{18:0}$= -25.9 ‰ (at the edge of the marine ellipse) could also correspond to a purely marine signal possibly suggesting that the proportion of marine oil/fat is underestimated with an uncertainty over 60 %. The ^{14}C dates presented a percentage of marine fats of ca. 65 % however, based only on one marine organism and two (non-identical reference measurements) this estimation by the ^{14}C method is not completely reliable. Alike ΔR determinations multiple ^{14}C measurements on reference organisms are required for a precise estimate of the percentage of marine products present in the TLEs. In order to illustrate the possible underestimation of marine fat/oil, a 100 % marine resource with 10 % error was implemented in the calibration of BN-110, falling in the range 854 – 1,110 AD (95% probability) after calibration (Figure 7-12). This result agrees better with the calibrated range of the terrestrial organism BN-MB-8 and BN-MB-10 of the same context than the previous correction and could support the ineffectiveness of the mixture estimation when marine products are dominant (i.e. $\%_{Aqua}$ > 50 %).

These two examples suggest a dominance of marine fat/oil in the TLE can produce less reliable correction and calibration of the CSRA dates.

7.5.2.4 Summary

The percentage of marine product calculated used the $\delta^{13}C$ values on the FAs showed overall a good compatibility with the percentage calculated using the ^{14}C values as end-member. The estimates of the percentage of marine products obtained using radiocarbon dates gave smaller errors, however, in most cases, the percentage of aquatic fat/oil calculated by both methods and

either adipose or milk end-members gave identical results (within error), due to the large uncertainties. In instances where the quantification of marine resources rather than a calendar age is needed then the ^{14}C method could be used as a tool to quantify such mixtures with more precise estimation (based on multiple ^{14}C dates recorded on terrestrial or marine organisms).

The results presented above support the possibility to use the $\delta^{13}C$ values on the FAs to correct for MRE in potsherds. Nonetheless is was raised that the non-homogeneity of lipid distribution in the clay could lead to erroneous estimation of the marine component. Therefore, in future dating programs the $\delta^{13}C$ values and CSRA dates on the FAs should be recorded from the same TLE to prevent this issue linked to the partitioning of lipids in the potsherds. The estimation of marine products using the $\delta^{13}C$ values could also, be limited by a lipid extract dominated by the marine over the terrestrial component due to the wide range of $\delta^{13}C$ values of reference UK marine organisms which can bias the quantification of marine products. If possible and in certain cases the end-members values should be re-evaluated for particular locations as an attempt to obtain more precise end-members and avoid such problem.

Nonetheless the corrected ^{14}C dates for the MREs and their calibrations at the site of Bornais showed that $\delta^{13}C$ values could be used to estimate the proportion of marine resource processing in potsherd, providing valid results for $\%_{marine} < 50$ %. The precision of the calibration will depend mainly on the uncertainties associated with the percentage of mixture calculated. The results demonstrated that there is no significant difference in the use of ruminant adipose or dairy $\delta^{13}C$ values for the percentage of marine resource. In practice, one is chosen over the other based on the $\Delta^{13}C$ values to approximate better 'real' end-members of animal products used in the vessels at the time (i.e. dairy or meat). A knowledge of local reservoir effects is also important especially if the organisms are likely to be affected by several MREs (as the

potsherds from layer BCC could suggest it), in which case, an appropriate representation of each MRE in the pot lipids should be used for the correction.

7.5.3 Calibration of the mixed marine/terrestrial products at Cliffs End farm

7.5.3.1 Quantification, correction and calibration of CSRA on FAs showing mixing of terrestrial and marine fats/oils

This part applies the findings of the previous section for the correction of the suggested MRE affecting the radiocarbon dates of lipids extracted from the potsherds from Cliffs End Farm obtained in Chapter 4 (Table 4-6). This reference site was the only one which failed application of the new CSRA method, therefore, the $\delta^{13}C$ method is used for the quantification the mixing of terrestrial and marine fats/oils and correction the CRSA measurements on potsherds from Cliff End Farm.

End-members for the terrestrial and marine organisms used were taken from the UK values published in Copley *et al.* (2003) and Cramp *et al.* (2014a). In the case where potsherds displayed $\Delta^{13}C$ values > - 3.1 ‰ the ruminant adipose values were used as the end-member and the dairy values being used for those with values < - 3.1 ‰ for the other one (excluding CEF-C-6471 dated by only one target; Table 7-7). As the MRE could not be determined due to the lack of marine remains recovered at the site, a ΔR of -57 ± 42 was used, as suggested by Russell *et al.* (2015) for the same time period of Cliff End Farms settlement.

Table 7-7: Evaluation of the % of aquatic fats/oils in potsherds from Cliffs End Farm using stable carbon isotope analysis of individual FAs.

Sample	$\Delta^{13}C$ (‰)	$\%_{Aqua}$	Age after correction cal BC (95 % probability)	Age of visible residue cal BC (95 % probability)
CEF-C-6460	-4.4	20 ± 27	800 – 652 BC	758 – 419 BC
CEF-C-6468	-2.5	28 ± 35	1,285 – 933 BC	995 – 829 BC
CEF-C-6470	-1.4	25 ± 29	1,105 – 949 BC	1,001 – 841 BC

Both potsherds CEF-C-6460 and CEF-C-6470 showed calibrated ages, after correction, in the lower range of the age of the visible residues associated with the same vessels (Table 7-7).

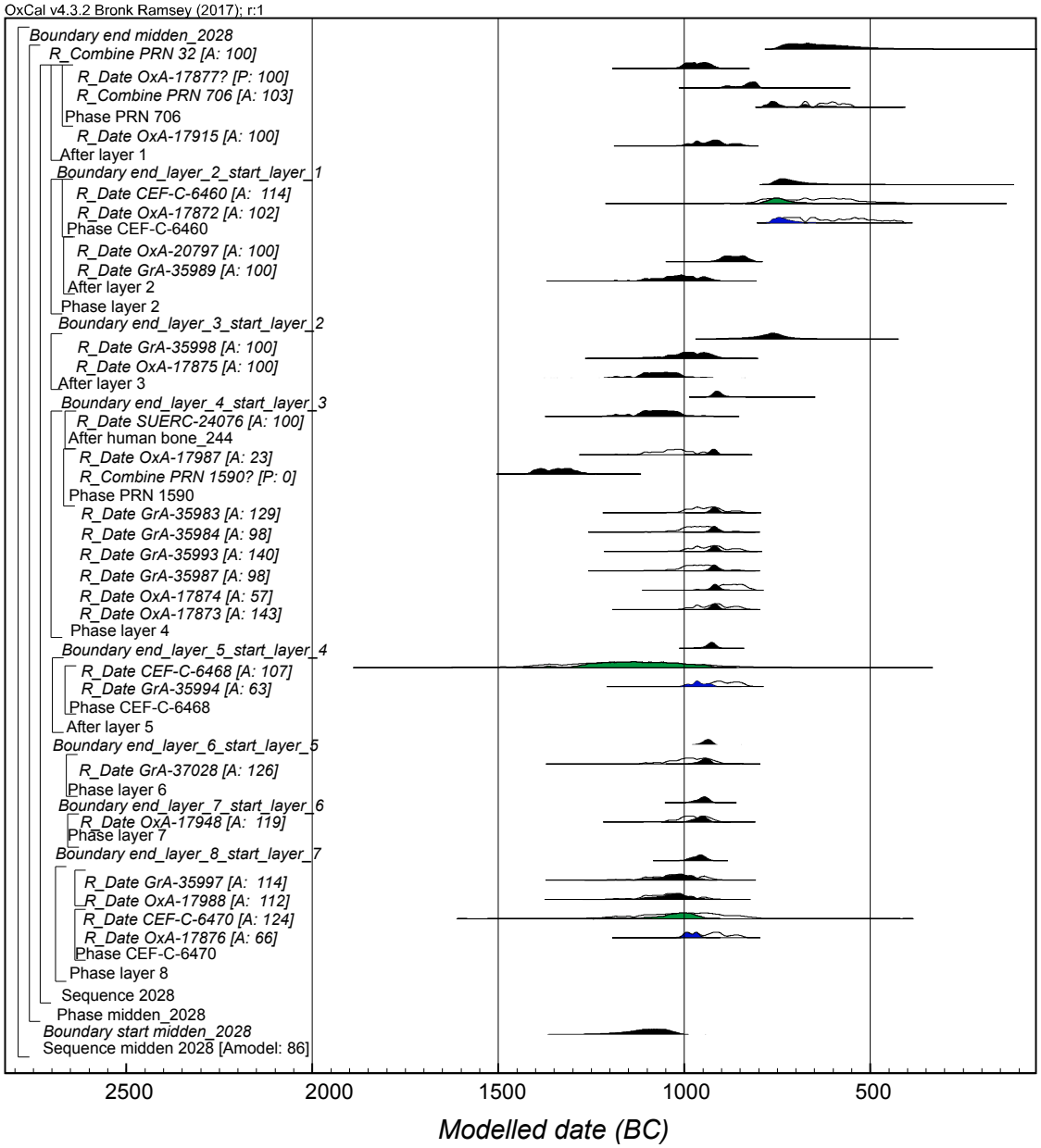

Figure 7-15: Probability distribution of all the dates used in the modelled sequence and of dates from lipids extracted from 4 pottery vessels. The distributions (representing the probability of an event to occur at a specific time) plotted in green correspond to the dates on absorbed residues, in blue those corresponding to the associated visible residues, in black the output of the model and other reference dates. Courtesy of Professor A. Bayliss for OxCal code (v4.3, Bronk Ramsey 2009; InCal13, Reimer *et al.* 2013).

Potsherd CEF-C-6468 calibrated to 1,366 – 944 BC exhibit an older age than the visible residue, which was calibrated to 995 – 829 BC, with a minor overlap of ca. 50 years at the end

of the calibration. This could reflect the dating of two different events by both residues. However, this potsherd seems to be dating an event older than anything else at the site suggesting an inappropriate correction for the MRE in this sherd, possibly related to the inhomogeneity of lipid deposition on different parts of the potsherd.

The ^{14}C ages of pottery vessels corrected for the reservoir effect were included in a CEF mathematical model similar to the one performed in Chapter 4 (with the exclusion of CEF-6471; Figure 7-15). The output ($A_{model} = 86$) shows the start of the period of the midden pit 2028 at 1156 – 1025 cal BC (68 % probability) and 1336 - 992 cal BC (95 % probability), which is in good agreement with the pre-existing model, which dated the start of the pit at 1175 – 1017 cal BC (68 % probability) and 1457 - 985 cal BC (95 % probability). This agrees with the literature, which dates the appearance of such type of pot during the 12th -11th century BC (Best *et al.* 2012; Marshall *et al.* 2012). The median values of the key parameters differ by an average of 6 years with a maximum of 26 years (Appendix 6.3).

7.5.3.2 Discussion

The correction of the MRE at Cliffs End Farm was successfully carried out using $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values to estimate the marine fat/oil component in the lipid residue and an ΔR from the literature. Here, only the potsherd CEF-C-6468 still exhibited an older age after correction, which suggests that correction for the MRE was not entirely appropriate in this case. This could be related to the non-homogeneity of lipid distribution in the potsherd. Overall, the revised model of CEF agrees with the published model, supporting that MRE in pottery lipids was corrected with a relevant quantitative estimate of the marine fat/oil contribution and local reservoir effect.

7.6 Conclusion

This chapter demonstrates the complexity of radiocarbon dating potsherds which contain aquatic products. Firstly, at the site of Bornais, the use of marine products was highlighted by both the faunal record and the lipid residue analysis which comprised mixed profiles of marine and terrestrial carcass/dairy products. The radiocarbon dates on pottery vessels confirmed by the presence of these marine/terrestrial mixtures with intermediate radiocarbon ages, occurring between the terrestrial and marine fats/oils, even in pottery vessels where aquatic biomarkers were not seen. In addition, the difference of the FAs abundances in fresh marine and terrestrial organisms does not appear to significantly affect the CSRA dates of individual FAs as most of the potsherds successfully passed the internal criterion.

Because there is a correlation between enriched $\delta^{13}C$ values and apparent MRE in the potsherd, the FA $\delta^{13}C$ values proved useful in estimating the percentage of marine fat/oil in a potsherd TLE. However, care must be taken with a marine contribution of >50 % as any discrepancy in the calculation, based on the wide range of values for the UK reference marine $\delta^{13}C$ values, may not accurately reflect the local diet. It was also determined that the same TLE must be used for both $\delta^{13}C$ and ^{14}C determinations, because lipids may be unevenly distributed across a vessel. Using different TLEs for $\delta^{13}C$ and ^{14}C determinations may result in differing values, caused by varying percentages of marine/terrestrial products deposited.

The calculation of the local reservoir effect at Bornais provided results which agreed with the previously reported literature values for the same spatiotemporal area. One of the phases, however, showed three different MREs which suggested that marine shells were collected from two different areas. In such cases, an estimate of the contribution of the individual MREs to the potsherd date should be considered to allow the most relevant correction of the dates to be

achieved. Here, after correction for the MRE, ^{14}C determinations from the potsherds were in good agreement with other dates from the settlement of Bornais. The second case study using the site of Cliffs End Farm, further demonstrated that the MRE accounted for the phenomenon encountered in Chapter 4 of the adsorbed residues showing older ages than the visible residues from the same sherd and that the ^{14}C dates of the adsorbed residues in pottery vessels can be corrected.

Significantly, it has been shown that lipids extracted from pottery vessels at coastal sites can be CSRA dated if the proper corrections are applied to the radiocarbon determinations. This requires:

(i) The use of an appropriate ΔR for the spatiotemporal area, and, where several MREs are revealed, caused by several collection areas for the marine organisms, the definition of each MRE contribution in the TLEs;

(ii) $\delta^{13}C_{16:0}$ and $\delta^{13}C_{18:0}$ values, ideally recorded from the same TLE as that used for ^{14}C dating, can be used to determine the percentage of the marine fats/oil in the TLE.

(iii) The use of end-members values for the terrestrial and marine products processed in pots (e.g. chose the $\delta^{13}C$ values of dairy values for potsherds which $\Delta^{13}C < -3.1$ ‰ and adipose values otherwise), by using either those of the database for UK animals (Copley *et al.* 2003; Cramp and Evershed 2014) or values recorded from reference animals representative of other environments (e.g. arid environments, Dunne *et al.* 2012).

Chapter 8.

Overview and future work

Chapter 8. Overview and recommendations for future work

8.1 Compound-specific radiocarbon dating of pottery vessels

Pottery vessels are widely recovered at archaeological sites and are thus used to establish relative chronologies, however, their accurate radiocarbon dating has long been challenging. To date, few attempts have been made to date absorbed lipid residues (Stott *et al.* 2001; Berstan *et al.* 2008), as opposed to visible residues or pottery temper, but these were only partially successful. Building on previous work initiated by Stott *et al.* (2001), this project has established a methodology which allows accurate radiocarbon dating of pottery lipids, providing, for the first time, a way of reliably dating archaeological vessels.

Advances in ^{14}C dating mean that high precision measurements on reduced sample sizes allows the dating of archaeological artefacts at the molecular level (Eglinton *et al.* 1996; Synal *et al.* 2007; Santos *et al.* 2010; Cersoy *et al.* 2017). A compound-specific radiocarbon dating technique using preparative capillary gas chromatography (PCGC) was recognised to be suitable for dating pottery vessels from its lipids residues (Stott *et al.* 2001; Berstan *et al.* 2008). The method, which specifically focussed on the isolation of animal products, used PCGC required the rigorous identification, quantification and elimination of exogenous contaminants prior to its application to well-dated pottery vessels.

In addition, the body of knowledge built over the years in the Organic Geochemistry Unit on lipid residue analysis of archaeological pottery provided a unique background experience to securely develop the CSRA dating of lipids. It allowed the detection of pottery with high lipid concentrations suitable for dating, the establishment of sampling strategies and the evaluation of a potential reservoir effect.

For this project, a total of 100 potsherds were selected for ^{14}C dating, making this the largest set of pottery vessels ever analysed by CSRA (summary of sites analysed in Figure 8-1).

Figure 8-1: Map summarising all the archaeological sites analysed in this thesis and their approximate age.

Those potsherds derive from diverse environments and burial contexts, and had an age range spanning from ca. 7,200 BP to the present day. Excluding sherds which exhibited low lipid recoveries or only yielded only one target, statistically consistent pairs of measurements were successfully obtained on 80 % (n = 55) of the potsherds dated by both $C_{16:0}$ and $C_{18:0}$ FAs. The method, therefore, gave extremely good results. Significantly, the results obtained in this thesis

represent the first accurate radiocarbon determinations on lipids preserved in pottery vessels with equivalent accuracy to other traditionally dated samples. These technical advances brought pottery vessels into the range of archaeological materials datable by radiocarbon analysis on a routine basis.

8.2 Summary of the main findings of the thesis

8.2.1 Methodological considerations for compound-specific radiocarbon dating (Chapter 3)

Compound-specific radiocarbon dating of FAs was performed using the PCGC instrument. First, method parameters involving column specifications and TLE concentration were explored with the aim of isolating 200 μg of C from FAs preserved in one pottery vessel in one day. In addition, a simple mass balance for the correction of the derivative carbon added during the derivatisation was tested and deemed able to provide high precision dates.

Furthermore, sources of exogenous contamination associated with the isolation procedure in the PCGC instrument were identified, assessed and step taken to eliminate them where required. The first contamination considered corresponded to column stationary phase degradation products associated with the isolated FAMEs. A new method using a uniquely suited high field NMR instrument at 700 MHz permitted the direct identification and quantification of the 'bleed' products, which were found to be negligible. Secondly, the organic solvent used to recover the isolated FAMEs from the traps was shown to be significant and eliminated by the introduction of a new solventless trap design. A glass wool plug introduced into the new traps provides a surface for eluting compounds to condense on, such that the target compound can be physically removed from the trap by pushing the glass wool plug out directly into a tin/aluminium capsule with a pipette. This recovery method turned out to be faster than

the solvent-based approach and avoided isolated FAMEs from contamination, e.g. via exposure under a blow down. Finally, a new cleaning method involving the heating of cold-spots (using a heat gun) was established to prevent cross-contamination ("memory effects") in the instrument. These new methodologies were systematically tested using standard FAMEs and were shown to meet the demands for optimal accuracy required for high precision archaeological dating.

8.2.2 CSRA of archaeological materials and pottery vessels from well-dated sites (Chapter 4)

A range of archaeological materials of known age were used to test the improved CSRA method. Firstly, archaeological fats from bog butter (covering a 3,000-year age range) showed an extremely good correlation between their bulk and CSRA uncalibrated dates. It showed that statistically identical measurements from two single compounds ($C_{16:0}$ and $C_{18:0}$ FAs) isolated from the same matrix could be obtained and be used as an internal quality control of the CSRA.

Several potsherds from known age sites of different age and burial environments were then successfully dated. These consisted of pottery vessels from: (i) the Sweet Track, England, preserved in a wetland area, and dated dendrochronologically from 3,807/6 BC, (ii) Takarkori Rockshelter, an arid site in the Libyan Sahara, dated *ca.* 5,200 BP, (iii) Çatalhöyük, Turkey, which was the oldest pottery, dated *ca*. 7,200 BP and (iv) Cliffs End Farm, England, which pottery was extremely well-dated from *ca* 3,000 BP (using bones and surface residues). The results obtained from each site correlated well to the available dates (including the Bayesian statistical model at Çatalhöyük) and represented the first accurate ^{14}C age determination on potsherd lipids. Nonetheless, the last site exposed the problem of the processing of aquatic products, which can bias the dating due to the marine reservoir effect (MRE). In addition, the

concentration of FAs required to permit the ^{14}C dating of sherds (with minimum destruction) was determined to be > 500 $\mu g.g^{-1}$ of sherd.

8.2.3 From lipid residues analysis to CRSA of pottery vessels in Neolithic Alsace (Chapter 5)

The ORA of 871 potsherds from the Alsace region highlighted the difference in dietary practices between the two regional LBK groups and later cultures. The LBK groups in the Upper Alsace showed an economy relying on both meat and milk. In the Lower Alsace, however, limited evidence for dairy practices was apparent with the LBK (ca. 5500 BP) and the Middle Neolithic group of the Grossgartach (ca. 5800 BP) but became widely established with the middle Neolithic group of Roessen (ca. 5900 BP).

This regional scale analysis demonstrated how to use lipid results from a pottery assemblage for the selection of sherds for a dating programme. From the study, found that approximatively 10 times the number of sherds to be dated should be analysed by ORA, as not all sherds yield sufficient lipid for dating, and this varies from site-to-site depending on lipid concentrations and recovery rates. It also highlighted that different vessel types could be a factor in selecting sherds suitable for radiocarbon dating; cooking pots with high lipid concentrations are the best candidates for radiocarbon dating.

Furthermore, the use of ORA with the faunal remains can help highlighting a potential reservoir effects at the sites studied. New radiocarbon dates were generated for the Alsatian Neolithic and their uncalibrated measurements on the LBK and Middle Neolithic groups were statistically consistent with the reference dates on bones and visible residues (Denaire *et al.* 2017). The dates on the Middle Neolithic group from the Grossgartach appeared to be compatible with the regional Bayesian statistical model.

8.2.4 CSRA of dairy residues in archaeological pottery vessels (Chapter 6)

The CRSA method was applied to archaeological questions and showed the utility of CSRA as quality control with the example of an ethnographical site which ORA results could only be explained with a radiocarbon date. A few sherds showed the presence of dairy residues in pottery vessels despite a strong cultural prohibition (Grillo 2014). These sherds were demonstrated to be older than anticipated, i.e. not modern, as they were dated from an historical period, explaining the seemingly ambiguous ORA findings.

Then pottery vessels from the LBK containing some of the earliest milk residues in Europe were successfully dated. The earliest dates on milk fats dated from the 53rd century BC are coherent with the LBK population, as the dates generated are younger than the formative/earliest LBK in the Hungarian region (Jakucs *et al.* 2016; Denaire *et al.* 2017). The earliest dates for dairying were obtained from the Upper Alsace region then Paris Basin, Netherland and Germany. The latest dates were obtained for the Polish site of Ludwinowo suggesting different routes of diffusion of the practice. More data on other LBK sites are, however, required to increase the precision and understand better the emergence of dairy practices but this example shows the impressive utility of CSRA dates on pottery vessels to answer archaeological questions.

8.2.5 CSRA of aquatic resources processing in archaeological pottery vessels (Chapter 7)

It was hypothesized that the processing of aquatic commodities in archaeological ceramics might influence potential radiocarbon dates, due to the reservoir effect. Consequently, the new CSRA method was applied to pottery from a coastal site with clear evidence of the exploitation

of marine products, to understand how this would influence the radiocarbon dates (Sharples forthcoming). ORA at the site of Bornais revealed the processing of ruminant products (carcass or dairy) and marine products in the same pottery vessels. The dating of terrestrial and marine animal remains permitted calculation of an average ΔR of -65 ± 46 for the East coast of the island. The dates obtained on the lipids extracted from the Bornais pottery vessels confirmed the mixing of marine and terrestrial commodities as intermediate dates between the ages of terrestrial and marine commodities were obtained.

The percentage of marine products in pots were calculated using both ^{14}C dates and $\delta^{13}C$ values with the latter giving wider estimation of the percentage of marine fat/oil contributing to the residue. These values largely agreed, except where a low number of dates were available (incorrect estimation of the MRE) or when there was an inhomogeneity of marine/terrestrial lipid deposition in a potsherd; the latter emphasising the importance of using the same TLE for both ^{14}C and $\delta^{13}C$ determinations. It was confirmed that the $\delta^{13}C$ values of FAs from equivalent modern reference animals can therefore be used as end-members to estimate the percentage of marine versus terrestrial fats/oils in a potsherd prior to calibration. Using an appropriate ΔR and percentage of marine fat/oil in the lipid extract, the calibration of CSRA dates corrected for the MRE gave coherent results for the settlement at Bornais.

Such a calibration was also successfully applied to the site of Cliff End Farm, which, after correction of the MRE, gave results consistent with the pre-existing statistical dating model. Significantly, the potential limitation of the CSRA method for sherds from sites which may display a reservoir effect, can be overcome, further emphasising the usefulness of potsherds for dating.

8.3 Recommendations for future work

The first results of the method for the routine dating of pottery vessels raised further questions and also avenues of exploration for developing the CSRA technique.

8.3.1 CRSA of pottery vessels from other known age sites

Archaeological sites of known age from other continents (Asia, America etc) could be dated to extend the spatial range of reference pottery vessels and demonstrate the universal applicability of the method. Also, sites with pottery vessels dated over 13,000 BP from Russia, China or Japan could be targets for dating (O'Malley *et al.* 1999; Wu *et al.* 2012; Yoshida *et al.* 2004). This would allow the application of the technique on the oldest known pottery in the world.

8.3.2 Extend the chronological and spatial resolution of the dating of the early exploitation of dairy products

The work performed on the direct dating of dairy product residues could be extended to more LBK sites in central Europe to obtain better chronological resolution. As suggested in Chapter 6, these chronological data could be correlated with the spatial distribution of milk residues together with LP evolution in Europe. Mathematical modelling could be performed to provide a better understanding of the emergence of dairying related to the evolution of the gene covariant -13,910T*. In addition, such dating could be extended to other regions, such as Anatolia or the Adriatic, where dairying was detected in early Neolithic cultures.

8.3.3 CSRA of cultures/sites only defined by pottery

In the archaeological record, it is not unusual to find pottery used by more mobile cultures which do not have their own settlements, but their characteristic artefacts are discovered associated with the settlements of other cultural groups. This is the case of La Hoguette or Limbourg, ceramics which were recovered associated with LBK assemblages from Paris Basin to Germany (Jeunesse 1987). These pottery vessels are often poorly dated, thus a direct radiocarbon date on food residues would provide valuable information on the span of the culture. Also, there are sites with a dearth of organic materials, such as Sierentz (Alsace, France), where no organic material, such as bones or wood, survived, due to soil acidity. Such sites could, therefore, be dated from their pottery vessels by CSRA.

8.3.4 Use of CSRA measurement to detect low-level marine products processing

In Chapter 7 it has been shown that potsherds with a mixed marine/terrestrial signal effect show ^{14}C measurements with a reservoir effect even in cases where no aquatic biomarkers in the TLEs are detected. Therefore, radiocarbon could be used as a tracer to detect and quantify fish/shellfish processing, even at low level, in pottery vessels recovered from coastal sites, where no other evidence (e.g. biomarkers) is present. Detection of reservoir effect in potsherds requires ^{14}C measurements on terrestrial materials from the site and identify any age deviation in the CSRA of lipids in pots from these measurements. The knowledge of reservoir effect at the site is also required to be able to quantify the amount of marine resource in the pot leading to such deviations. This method would allow a more precise estimate of the percentage of marine products processed in pots than the use of $\delta^{13}C$ values on both FAs.

8.3.5 The use of gas source for dating sherds with low lipid concentrations

One limitation of the CSRA technique is the concentration of lipids required to date pottery vessels (minimum 500 $\mu g.g^{-1}$ of sherd). In order to extend the technique to the dating of sherds containing lower concentrations of lipids in pottery, with minimal destruction of vessels, the use of the gas ion source could be considered. The gas source is able to measure smaller samples sizes (< 100 μg) directly as CO_2, instead of using a graphite target, and thus could possibly offer a solution. The dates obtained would, however, show greater uncertainties than with using the conventional graphite system, but may still be of value depending on the question being addressed.

Before testing this method on archaeological materials methodological assessments concerning the minimal amount of C which can be determined with acceptable uncertainty and background, need to be performed using standard AMS materials (similarly to the assessments performed in Chapter 3). This would allow the evaluation of whether such an analysis could be used at sites where potsherds from the assemblage have low lipid concentrations but for which no other datable materials are available.

8.3.6 CSRA of unsaturated fatty acids

Some of the compounds identified in organic residue analysis are known to have an ambiguous origin, i.e. possibly suggesting contamination, e.g. contamination from the handling (cholesterol derivatives, squalene) or from the storage of potsherds (plasticisers; Evershed 1993). This is especially the case for the (unsaturated) $C_{18:1}$ fatty acid which is abundant in fresh fats, but is highly prone to oxidation and therefore does not survive well in archaeological contexts (Evershed 1993). If this is identified in potsherd lipids in high concentrations, then it throws into question the archaeological age of the $C_{16:0}$ or $C_{18:0}$ fatty acids. Is this proof of

modern contamination or particularly well-preserved fats? For instance the dating of the ethnographic sherd from Lakaterny (Samburu, Kenya; Chapter 6, Table 6-1) showed the date of $C_{18:1}$ to be identical within error of the $C_{16:0}$ and $C_{18:0}$ FAs, proving their contemporaneity. The CSRA of the $C_{18:1}$ compared to the $C_{16:0}$ and the $C_{18:0}$ FA extracted from archaeological pottery vessels would thus be a good quality control and confirm whether the $C_{18:1}$ is modern (and therefore proof of contamination) or whether it is of archaeological age.

8.3.7 CSRA of other biomarkers recovered in archaeological pottery vessels

Biomarkers other than FAs can relate to other sources of food such as the presence of *n*-alkanes for beeswax (e.g. Heron *et al.* 1994) or for *Brassica* (cabbage; Evershed *et al.* 1991). The radiocarbon dating of other classes of biomarker could also be applicable to other environmental matrices, such as soils or sediments. Progress towards the dating of such biomarkers could require rigorous testing of protocols, e.g. GC column selection, temperature programme, and precise compounds, ideally two from each class to allow internal quality control to be applied, as has been shown to be so effective for pottery lipids. Evaluations of the new PCGC method will require careful selection of reference materials of different age range such as *n*-alkanes or vanillin (often used to evaluate PCGC performance e.g. Eglinton *et al.* 1996, Ziolkowski and Druffel 2009). The preliminary considerations gave a good correlation ($y = 1.0018x - 0.0021$; $R^2 = 0.9999$) between bulk and CSRA dates on a range of vanillin mixtures from modern to fossil (Figure 8-2) using the new S-Trap system and heat-based cleaning. While this has worked well for compounds with lower molecular weights than FAMEs, for higher molecular weight compounds the effects of changing temperature program or trapping windows will have to be assessed, e.g. possible co-eluting bleed products associated with trapped compounds will have to be identified and quantified to understand the influence of increased elution temperatures and the nature of stationary phase, *cf*. Chapter 3.

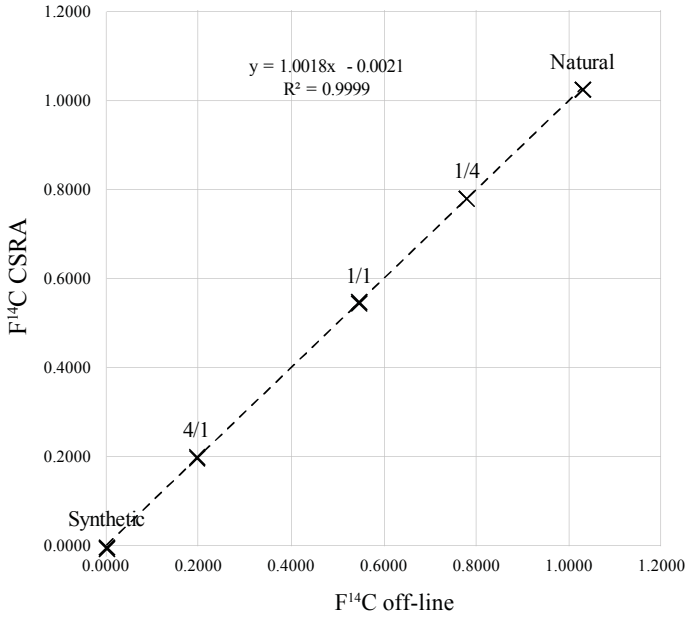

Figure 8-2: Fraction modern of vanillin mixtures (Synthetic/Natural ratio) CSRA dated plotted against their off-line fraction modern.

8.3.8 CSRA of other archaeological materials containing lipids

Lipids are also present in other archaeological materials. Similarly, to the attempts made to date seeds in this thesis (Chapter 4), CSRA dating of lipids from other materials could be carried out and be critically evaluated in terms of the mass of material required and the necessity of such dating as opposed to more conventional pre-treatments.

The dating of lipids from bones already well-dated (from collagen) could be performed to investigate whether this could be an alternative dating technique for bones with poorly preserved collagen, as opposed to CSRA dating the hydroxyproline isolated by HPLC as suggested by van Klinken and Mook (1990). Other materials could be targeted, such as lipids associated with the mummy bandages, which require isolation from the other organic materials present, such as bitumen (Buckley *et al.* 2004; Clark *et al.* 2013, 2016). Exceptional artefacts could also be CSRA dated, e.g. a Roman cream made from a mixture of inorganic and organic components, including animal fat (Evershed *et al.* 2004).

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Appendices

Appendix 1: Sample size study

Appendix 1-1: Magazine of (a) 1 mg, (b) 0.5 mg, (c) 0.2 mg and (d) 0.1 mg of C. Details of current, counts, $F^{14}C$ and Age BP for the OXA II, phthalic anhydride (used as blank), IAEA C7, IAEA C8 and $C_{18:0}$ FAME.

(a)

Sample	BRAMS #	Weight (µg)	^{12}C (µA)	^{14}C counts	$F^{14}C \pm 1\sigma$	Age $\pm 1\sigma$ (BP)
OXA II	1028.1.35	986	30.8	1,331,315	1.3403 ± 0.0031	-2,353 ± 25
	1028.1.36	992	30.2	1,311,535	1.3407 ± 0.0031	-2,355 ± 25
	1028.1.37	985	28.8	1,245,022	1.3410 ± 0.0031	-2,357 ± 25
Phthalic anhydride	1029.1.22	997	29.1	2,605	0.0021 ± 0.0385	49,697 ± 310
	1029.1.23	983	30.4	2,568	0.0019 ± 0.0410	50,444 ± 330
IAEA-C7	1030.1.18	996	29.1	470,913	0.4963 ± 0.0033	5,627 ± 26
	1030.1.19	993	29.1	470,578	0.4958 ± 0.0033	5,635 ± 26
IAEA-C8	1031.1.18	974	30.7	151,050	0.1500 ± 0.0040	15,237 ± 32
	1031.1.19	987	30.5	181,200	0.1806 ± 0.0038	13,747 ± 31
$C_{18:0}$	1046.1.7	994	30.2	983,480	1.0347 ± 0.0031	-274 ± 25
	1046.1.8	994	29.4	954,581	1.0320 ± 0.0031	-253 ± 25

(b)

Sample	BRAMS #	Weight (µg)	^{12}C (µA)	^{14}C counts	$F^{14}C \pm 1\sigma$	Age $\pm 1\sigma$ (BP)
OXA II	1028.1.32	518	18.6	1,106,589	1.3394 ± 0.0031	-2,347 ± 25
	1028.1.33	518	18.6	1,109,275	1.3403 ± 0.0031	-2,353 ± 25
	1028.1.34	497	19.3	1,154,264	1.3423 ± 0.0031	-2,365 ± 25
Phthalic anhydride	1029.1.20	543	19.2	4,140	0.0043 ± 0.0210	43,842 ± 168
	1029.1.21	559	20.0	4,093	0.0039 ± 0.0226	44,471 ± 181
IAEA-C7	1030.1.16	529	20.0	445,911	0.4944 ± 0.0033	5,659 ± 27
	1030.1.17	520	18.2	402,411	0.4922 ± 0.0034	5,695 ± 27
IAEA-C8	1031.1.16	525	18.8	129,803	0.1507 ± 0.0042	15,202 ± 34
	1031.1.17	528	19.2	131,016	0.1495 ± 0.0042	15,267 ± 34
$C_{18:0}$	1046.1.5	501	18.5	824,669	1.0291 ± 0.0031	-231 ± 25
	1046.1.6	524	19.1	860,051	1.0334 ± 0.0031	-264 ± 25

(c)

Sample	BRAMS #	Weight (µg)	^{12}C (µA)	^{14}C counts	$F^{14}C \pm 1\sigma$	Age $\pm 1\sigma$ (BP)
OXA II	1028.1.29	216	11.5	421,686	1.3398 ± 0.0034	-2,350 ± 27
	1028.1.30	212	12.7	463,700	1.3428 ± 0.0034	-2,368 ± 27
	1028.1.31	206	12.2	444,942	1.3393 ± 0.0034	-2,347 ± 27
Phthalic anhydride	1029.1.18	209	12.2	2,175	0.0064 ± 0.0233	40,627 ± 187
	1029.1.19	227	12.9	2,033	0.0056 ± 0.0242	41,617 ± 195
IAEA-C7	1030.1.14	206	11.6	158,537	0.4957 ± 0.0040	5,637 ± 32
	1030.1.15	214	12.2	168,147	0.4964 ± 0.0040	5,626 ± 32
IAEA-C8	1031.1.14	199	10.8	46,034	0.1512 ± 0.0032	15,173 ± 50
	1031.1.15	204	11.0	46,758	0.1516 ± 0.0062	15,156 ± 49
$C_{18:0}$	1046.1.3	218	11.7	321,593	1.0331 ± 0.0035	-262 ± 28
	1046.1.4	207	11.6	317,928	1.0351 ± 0.0035	-277 ± 28

(d)

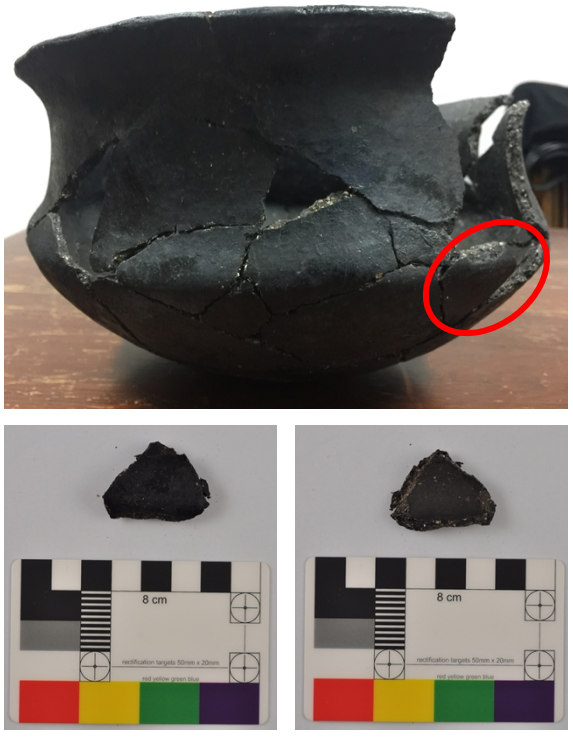
Sample	BRAMS #	Weight (µg)	^{12}C (µA)	^{14}C counts	$F^{14}C \pm 1\sigma$	Age $\pm 1\sigma$ (BP)
OXA II	1028.1.26	105	8.5	186,907	1.3409 ± 0.0040	-2,356 ± 32
	1028.1.27	105	8.5	187,988	1.3417 ± 0.0039	-2,361 ± 32
	1028.1.28	105	8.7	191,551	1.3394 ± 0.0039	-2,347 ± 32
Phthalic anhydride	1029.1.16	104	9.1	1,644	0.0112 ± 0.0253	36,090 ± 203
	1029.1.17	114	8.9	1,543	0.0107 ± 0.0262	36,458 ± 211
IAEA-C7	1030.1.12	84	7.0	58,571	0.4972 ± 0.0053	5,614 ± 43
	1030.1.13	98	7.8	64,894	0.4941 ± 0.0052	5,663 ± 41
IAEA-C8	1031.1.12	102	6.9	18,247	0.1513 ± 0.0087	15,171 ± 70
	1031.1.13	107	8.5	22,535	0.1519 ± 0.0080	15,141 ± 64
$C_{18:0}$	1046.1.1	105	8.5	142,699	1.0363 ± 0.0042	-287 ± 33
	1046.1.2	128	10.4	172,512	1.0370 ± 0.0040	-292 ± 32

Appendix 2: Sweet track, Somerset Levels, England

Appendix 2-1: Pictures of (a) SW1 rim and body sherds and (b) SW2 reconstructed and the sherd sampled.

(a)

(b)



Appendix 2-2: Details of lipid residue analysis of radiocarbon dated pottery vessels from the Sweet track. From Berstan (2002) and Berstan *et al.* (2008).

Sherd#	Description	C^o (µg.g^{-1})	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
SW1	Refitted, carinated bowl	13806	-30.1	-32.8	-2.7	Ruminant adipose fats
SW2	Full shape, carinated bowl	4900	-28.8	-33.6	-4.8	Dairy fats

Appendix 3: Takarkori Rock Shelter, Libya

Appendix 3-1: Details of lipid residue analysis of radiocarbon dated pottery vessel from Takarkori Rock Shelter. From Dunne (2014).

Sherd #	Layer	Description	Period	C^o ($\mu g.g^{-1}$)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
TAK21A	25	Single, decorated	MP	9503	-14.7	-20.5	-5.8	Dairy fats
TAK1572	245	Single, decorated	MP	3558	-23.7	-28.2	-4.5	Dairy fats

Appendix 3-2: Radiocarbon dates available for the Middle Pastoral period (MP) at the site of Takarkori Rock Shelter (from Dunne *et al.* 2012; Cherkinsky and di Lernia 2013; di Lernia and Tafuri 2013).

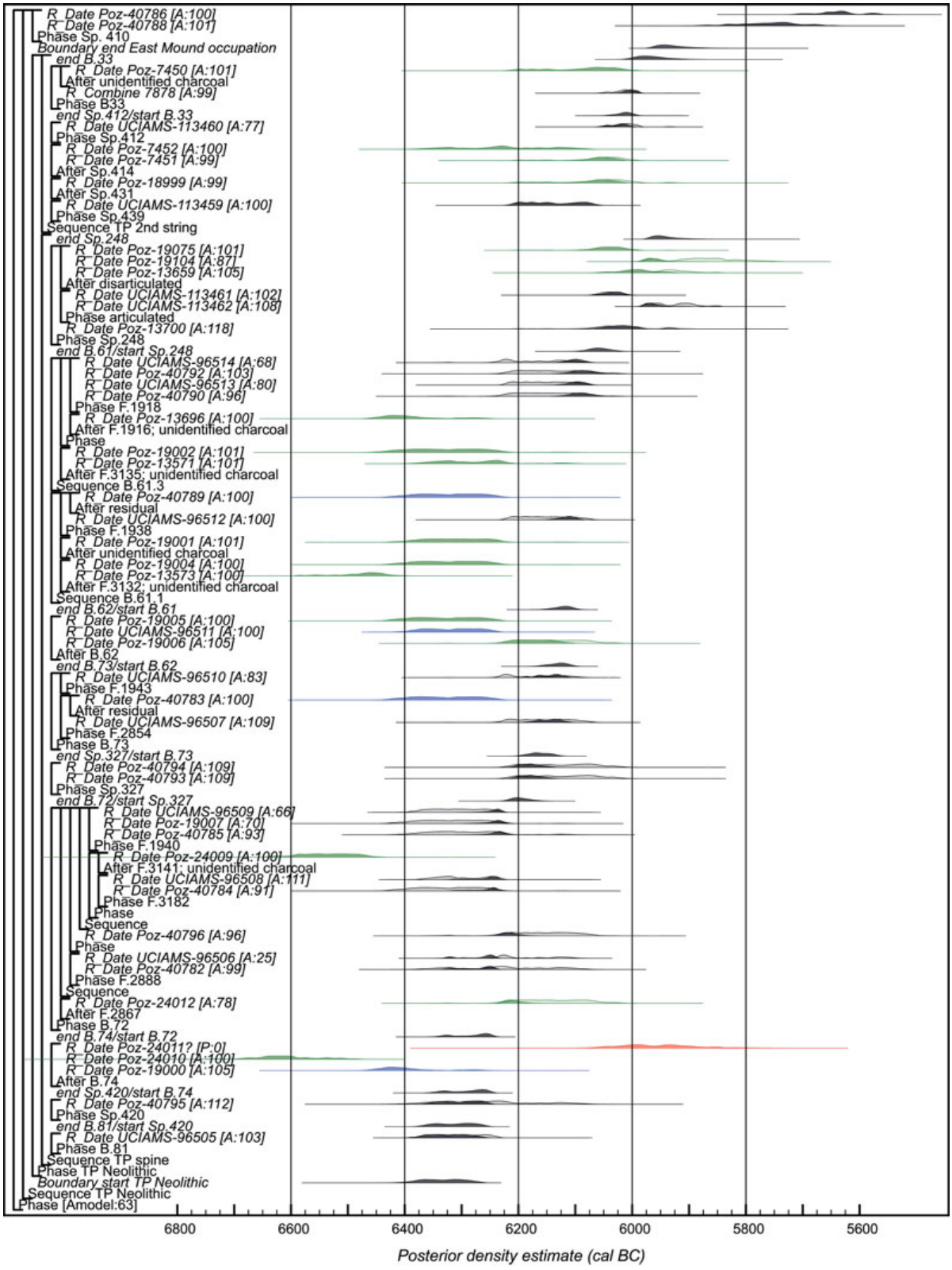
Lab #	Material	Layer	Subphase	Age ± 1σ (BP)	Calibrated age BC (95 % prob.)
UGAMS#8707	Seeds	-	MP2	4,970 ± 25	3,800-3,660
LTA907A	Charcoal	22	MP2	5,064 ± 55	3,970-3,710
LTL362A	Skin (sheep/goat)	-	MP2	5,070 ± 35	3,960-3,780
UGAMS#10149	Dung	330	MP2	5,170 ± 25	4,003-3,951
UGAMS#01843	Collagen	-	MP2	5,280 ± 50	4,240-3,980
UGAMS#01841	Collagen	25	MP2	5,340 ± 50	4,330-4,040
GX-31077	Bone collagen	H9	MP1	5,600 ± 70	4,600-4,330
LTL376A	Dung	-	MP1	5,980 ± 50	5,000-4,720
UGAMS#2852	Enamel biopatite	-	MP1	5,980 ± 70	5,050-4,710
GX-30324-AMS	Human bone	H1	MP1	6,090 ± 60	5,210-4,840

Appendix 3-3: Lipid concentration (Dunne 2014; Table A1.4) and radiocarbon measurements (Mercuri *et al.* 2018; Table 1 and BRAMS dates) on archaeological seeds from Takarkori Rock Shelter,

Sample #	Species	Layer	Period	C^o ($\mu g.g^{-1}$)	Lab #	Age ± 1σ (BP)
S1	*Urochloa*	FP267	MP2-LP1	540.9	LTL16530A	4,732 ± 45
					BRAMS-1433.1.1	5,007 ± 27
S2	*Echinochloa*	FP267	MP2-LP1	1376.9	LTL16530A	4,732 ± 45
					BRAMS-1434.1.1	5,031 ± 27
S3	*Setaria*	407	LA2	861.3	LTL15247A	8,256 ± 45
					BRAMS-1435.1.1	8,301 ± 30
S4	*Urochloa*	103	LA3	1714.5	LTL16091A	7,629 ± 55
					BRAMs-1436.1.1	7,720 ± 29
S5	*Echinochloa*	275	MP2-LP1	6122.8	LTL16094A	4,987 ± 45
					BRAMS-1437.1.1	5,010 ± 27
S6	*Urochloa*	132	MP1	2403.5	UGAMS#8706	5,660 ± 25
S12	*Panicum*	-	-	8970.9	BRAMS-1438.1.1	5,623 ± 27
S13	*Cyperacea*	FP28	MP2	2856.8	-	-
S14	*Colocynthis*	FP28	MP2	927.9	BRAMS-1440.1.1	4,928 ± 27
S15	*Sorghum*	L369	LA3	6267.8	UGAMS#8708	7,930 ± 30
					BRAMS-1441.1.3	7,988 ± 30

Appendix 4: Çatalhöyük East, Turkey

Appendix 4-1: Probability distribution of radiocarbon dates at the site of Çatalhöyük East modelled in OxCal v4.1. Probability distribution plotted outlined correspond to the simple radiocarbon calibration and the solid ones to the results of the model. The distributions plotted in black were fully included in the model, in green correspond to probable old wood effect, in blue are probably residual samples and in red are probably intrusive samples. From Marciniak *et al.* (2015, Figure 2).



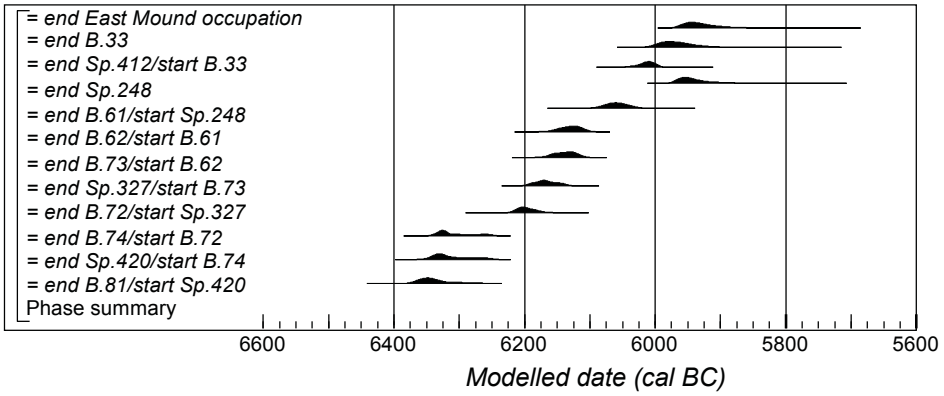
Appendix 4-2: Radiocarbon dates available for the TP area at the site of Çatalhöyük East. Adapted from Marciniak *et al.* (2015, Table 1).

Lab #	Unit #	Context	Level	Age ± 1σ (BP)	Inclusion in the model
UCIAMS-96505	15896	B81	M	7,430 ± 25	Fully included
Poz-40795	17600	Sp.420	M	7,380 ± 60	Fully included
Poz-1900	13533	B.74	N	7,539 ± 47	Probably residual
Poz-24010	15807	B.74	N	7,790 ± 50	Possible old wood effect
Poz-24011	15809	B.74	N	7,090 ± 70	Intrusive, excluded
Poz-40796	17630	B72	O	7,310 ± 50	Fully included
Poz-19007	13512	B.72	O	7,440 ± 50	Fully included
UCIAMS-96509	13512A	B.72	O	7,430 ± 30	Fully included
Poz-40785	13512b	B.72	O	7,410 ± 50	Fully included
UCIAMS-96508	15278a	B.72	O	7,405 ± 25	Fully included
Poz-40784	15278b	B.72	O	7,450 ± 50	Fully included
UCIAMS-96506	15829a	B.72	O	7,350 ± 25	Fully included
Poz-40782	15829b	B.72	O	7,360 ± 50	Fully included
Poz-24012	15827	B.72	O	7,270 ± 50	Possible old wood effect
Poz-24009	15204	B.72	O	7,700 ± 50	Possible old wood effect
Poz-40793	15839 1 (41) B18	Sp.327	O	7,250 ± 50	Fully included
Poz-40794	15839 3 (311) B28	Sp.327	O	7,250 ± 50	Fully included
UCIAMS-96507	15274a	B.73	P	7,310 ± 35	Fully included
Poz-40783	15274b	B.73	P	7,460 ± 50	Probably reworked
UCIAMS-96510	13504	B.73	P	7,335 ± 25	Fully included
Poz-19006	13050	B.62	Q	7,280 ± 50	Possible old wood effect
UCIAMS-96511	13029	B.62	Q	7,445 ± 30	Redeposited
Poz-19005	13030	B.62	Q	7,460 ± 50	Possible old wood effect
Poz-19004	12285	B.61	R	7,450 ± 50	Possible old wood effect
Poz-13573	11529	B.61	R	7,620 ± 50	Possible old wood effect
Poz-19001	11582	B.61	R	7,430 ± 50	Possible old wood effect
UCIAMS-96512	13023a	B.61	R	7,295 ± 25	Fully included
Poz-40789	13023b	B.61	R	7,450 ± 50	Probably reworked
Poz-19002	12244=11745	B.61	R	7,460 ± 70	Possible old wood effect
Poz-13571	12244=11745	B.61	R	7,390 ± 40	Possible old wood effect
Poz-13696	12259	B.61	R	7,530 ± 50	Possible old wood effect
UCIAMS-96513	12237	B.61	R	7,300 ± 25	Fully included
Poz-40790	12237=12248b	B.61	R	7,290 ± 50	Fully included
UCIAMS-96514	12243a	B.61	R	7,335 ± 30	Fully included
Poz-13700	11562	Sp.248	R	7,150 ± 50	Fully included
Poz-13569	11702	Sp.248	R	7,090 ± 50	Residual
UCIAMS-113462	11700	Sp.248	R	7,025 ± 20	Fully included
UCIAMS-113461	11571	Sp.248	R	7,175 ± 20	Fully included
Poz-19074	10986.X25	Sp.248	R	4,380 ± 90	Not Neolithic, excluded
Poz-19104	10986.X11	Sp.248	R	6,990 ± 40	Curated or residual
Poz-19075	10986.X29	Sp.248	R	7,180 ± 40	Curated or residual
UCIAMS-113459	17804.F1	Sp.439	N	7,265 ± 25	Fully included
Poz-18999	7840	Sp.431	O	7,183 ± 55	Possible old wood effect
Poz-7451	7866 (TOP)	Sp.414	Q	7,190 ± 40	Possible old wood effect
Poz-7452	7866 (BOTTOM)	Sp.414	Q	7,360 ± 50	Possible old wood effect
UCIAMS-113460	7867.f13	Sp.412	R	7,130 ± 20	Fully included
Poz-7449	7878	B.33	R	7,100 ± 50	Fully included
UCIAMS-113463	7878	B.33	R	7,145 ± 20	Fully included
Poz-7450	7484	B.33	R	7,210 ± 50	Possible old wood effect
Poz-40788	7867.F4&FF5	Sp.410	-	6,870 ± 50	Fully included
Poz-40786	7882.F12&F13	Sp.410	-	6,720 ± 40	Fully included

Appendix 4-3: Details of lipid residue analysis of radiocarbon dated pottery vessels from the TP area at site of Çatalhöyük East (Roffet-Salque and Evershed In press).

Sample	Context	Unit	Level	Pot shape	C^o ($\mu g\ g^{-1}$)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
TP.M12	Sp 420	17670	M	Single, bowl	115	-28.4	-28.8	-0.4	Ruminant adipose fat
TP.M17	Sp 420	17670	M	Single, deep jar	393	-24.1	-24.5	-0.4	Ruminant adipose fat
TP.M24	Sp 420	17617	M	Single, bowl	992	-25.9	-26.5	-0.6	Ruminant adipose fat
TP.N02	Sp 346	17809	N	Refitted, bowl	362	-25.2	-26.6	-1.3	Ruminant adipose fat
TP.N10	Sp 346	17809	N	Refitted, deep jar	575	-25.3	-27.0	-1.7	Ruminant adipose fat
TP.O02	B72	17630	O	Single, bowl	147	-24.3	-25.9	-1.6	Ruminant adipose fat
TP.O09	B72	17630	O	Refitted, bowl	310	-25.3	-26.3	-1.0	Ruminant adipose fat
TP.O15	B72	15839	O	Refitted, deep jar	327	-24.3	-25.5	-1.2	Ruminant adipose fat
TP.O23	B72	17630	O	Refitted, deep jar	1390	-25.2	-27.0	-1.8	Ruminant adipose fat
TP.P07	Sp.432	13522	P	Single, deep jar	640	-25.0	-27.8	-2.8	Ruminant adipose fat
TP.P13	Sp.432	13522	P	Single, deep jar	362	-22.3	-24.3	-2.1	Ruminant adipose fat
TP.P14	Sp.432	13522	P	Single, deep jar	715	-22.6	-25.9	-3.3	Ruminant adipose fat
TP.Q05	Sp 414	7841	Q	Single, deep jar	915	-24.7	-26.7	-2.0	Ruminant adipose fat
TP.Q06	Sp 414	7841	Q	Single, deep jar	331	-25.5	-27.4	-1.9	Ruminant adipose fat
TP.Q07	Sp 414	7841	Q	Single, deep jar	471	-24.3	-25.8	-1.5	Ruminant adipose fat
TP.R09	-	7867	R	Single, deep jar	986	-25.2	-26.5	-1.3	Ruminant adipose fat

Appendix 4-4: Summary of key dates parameters from the revised model of the TP area.

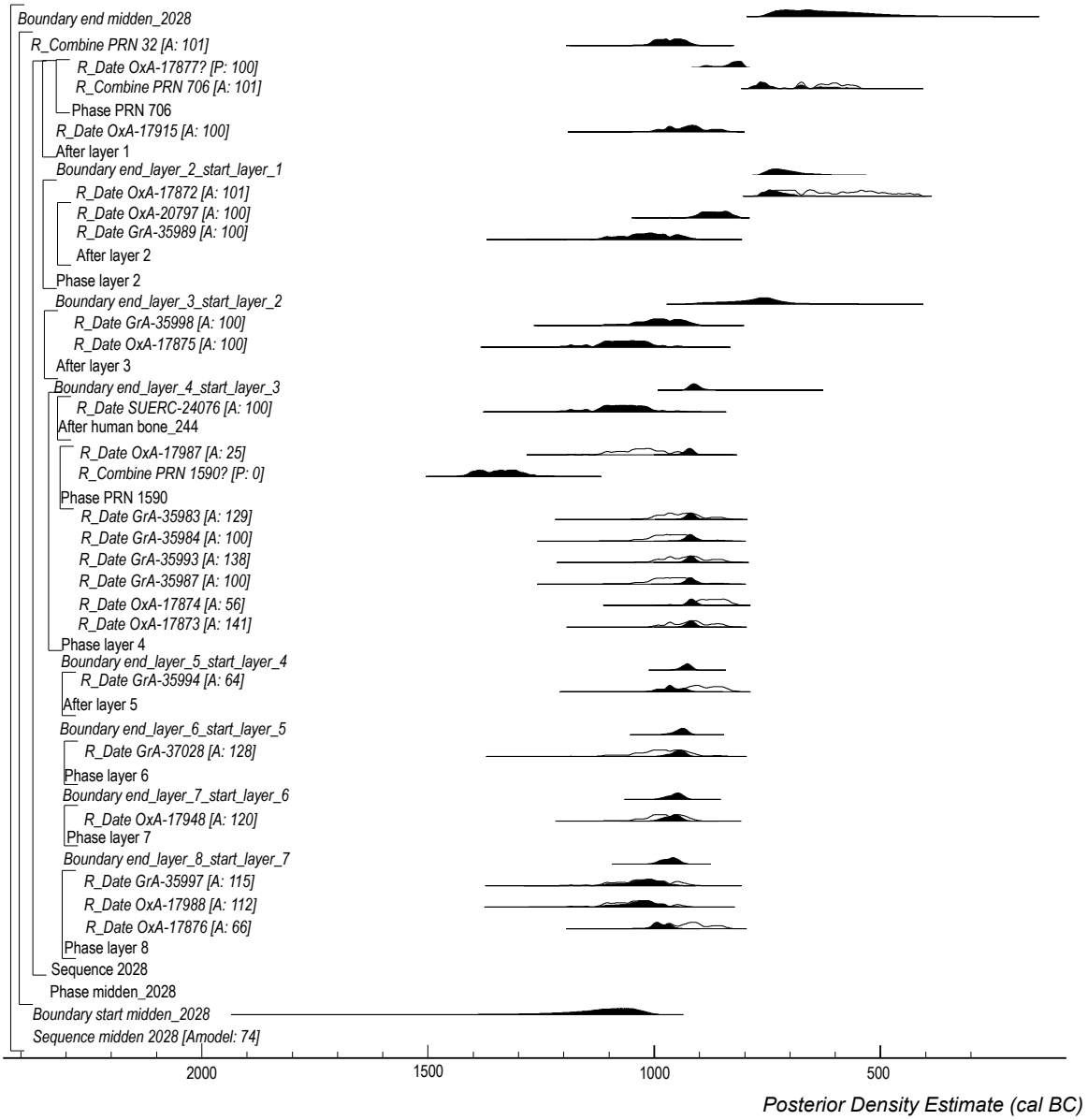


Appendix 4-5: Summary of key dates parameters median values for the original and revised model of the TP area.

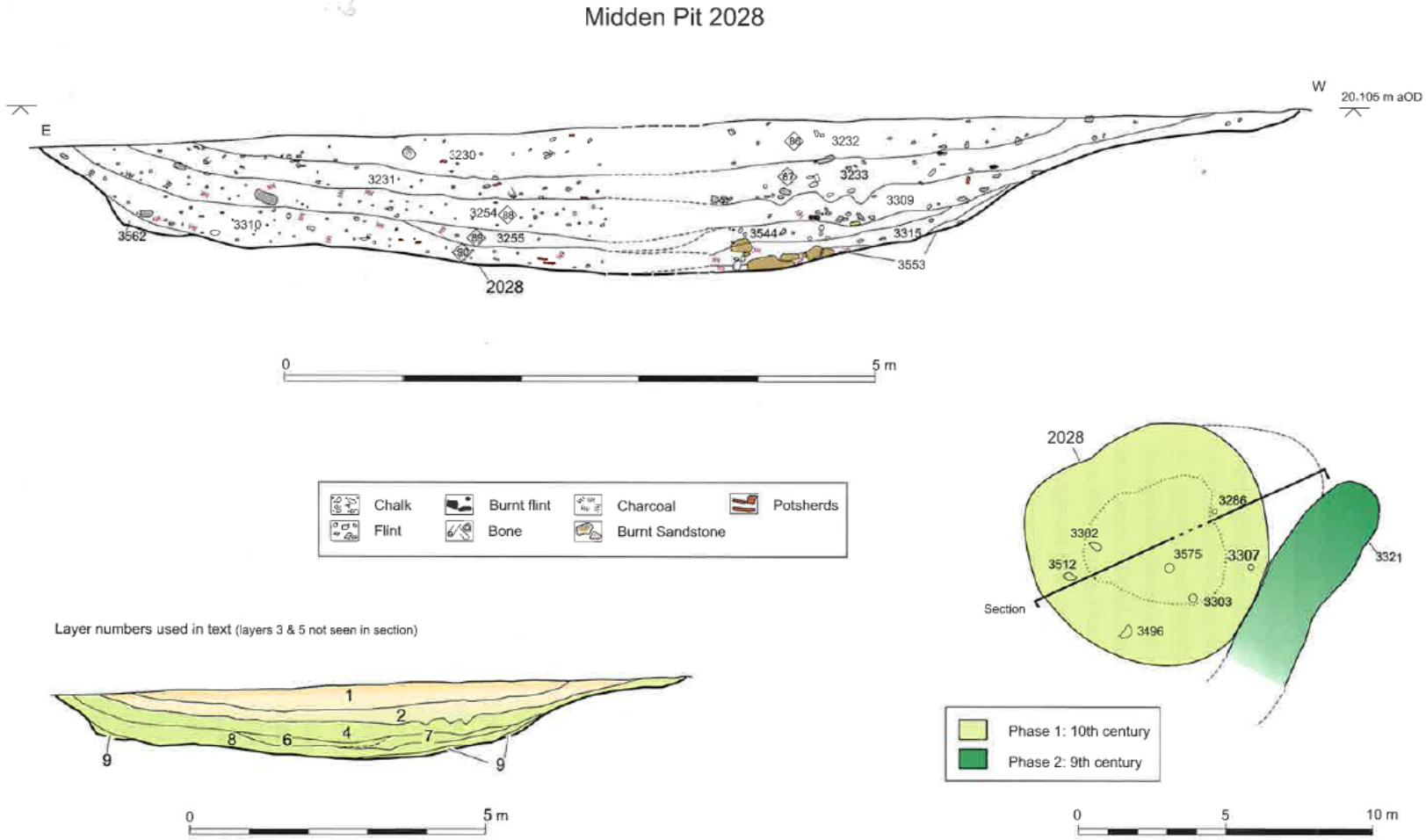
Key parameters	Original model	Model with lipid dates	
	Median (y BP)	Median (y BP)	Deviation from original model (y)
end B.81/start Sp.420	-6345	-6343	2
end Sp.420/start B.74	-6330	-6321	9
end B.74/start B.72	-6324	-6314	10
end B.72/start Sp.327	-6202	-6199	3
end Sp.327/start B.73	-6171	-6168	3
end B.73/start B.62	-6140	-6138	2
end B.62/start B.61	-6131	-6130	1
end B.61/start Sp.248	-6060	-6060	0
end Sp.248	-5944	-5947	3
end Sp.412/start B.33	-6012	-6013	1
end B.33	-5967	-5970	3

Appendix 5: Cliffs End Farm, Isle of Thanet, Kent, England

Appendix 5-1: Probability distribution of radiocarbon dates from the midden pit.2028 sequence. Probability distribution plotted outlined correspond to the simple radiocarbon calibration and in black the modelled one. From Marshall *et al.* (2014, Figures 3.10).



Appendix 5-2: Plan of midden pit 2028. From Leivers and McKinley (2014, Figure 2.7).



Appendix 5-3: Summary of key dates parameters median values for the original and revised model without and with reservoir effect correction at the site of Cliff End Farm.

Key parameters	Original model	Model with lipid dates non-corrected for reservoir effect (without CEF-F-6471)		Model with lipid dates corrected for reservoir effect (ΔR = -57 ± 42)	
	Median (y)	Median (y)	Deviation from original model (y)	Median (y)	Deviation from original model (y)
start midden 2028	-1114	-1129	15	-1106	8
end layer 8/start layer 7	-965	-965	0	-961	4
end layer 7/start layer 6	-953	-953	0	-950	3
end layer 6/start layer 5	-941	-941	0	-939	2
end layer 5/start layer 4	-929	-929	0	-928	1
end_layer_4/start_3	-911	-911	0	-911	0
end layer 3/start 2	-770	-819	49	-768	2
end layer 1/start 1	-714	-733	19	-720	6
end_midden_2028	-611	-649	38	-637	26

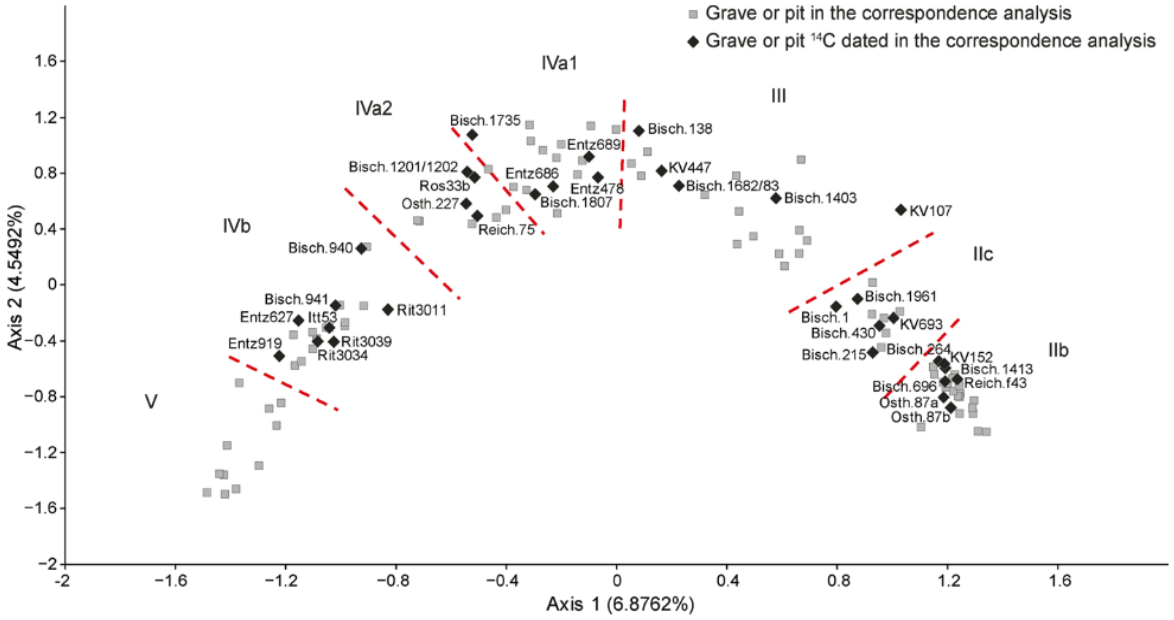
Appendix 5-4: Details of lipid residue analysis and radiocarbon dates on charred residues from pottery vessels from Cliffs End Farm.

Sherd #	Context /enclosure	Unit	Layer	Potsherd	Lab #	Age ± 1σ (BP)	C° (µg.g^{-1})	FAs	Aquatic biomarkers	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
CEF-C-6451	North	-	-	Single	OxA-18442	2,846 ± 29	39	C_{16}-C_{18}	-	-26.8	-28.8	-1.9	Mixture ruminant adipose/aquatic fats?
CEF-C-6452	North	-	-	Refitted	OxA-18443	2,793 ± 29	42	$C_{16,}$ C_{18}	-	-	-	-	-
					GrA-37697								
CEF-C-6453	North	-	-	Refitted	OxA-18441	2,865 ± 28	29	C_{16}-C_{22}	-	-	-	-	-
CEF-C-6454	North	2469	-	Refitted	GrA-37696	2,775 ± 30	306	C_{14}-C_{20}	APAAs, TMTD	-26.2	-27.9	-1.7	Mixture ruminant adipose/aquatic fats
CEF-C-6455	Central	2195	-	Refitted	OxA-18446	2,822 ± 29	45	C_{16}-C_{18}	-	-	-	-	-
CEF-C-6456	Central	2382	-		GrA-37715	2,740 ± 30	31	C_{16}-C_{18}	-	-	-	-	-
CEF-C-6457	South	3153	-	Refitted	OxA-18719	2,842 ± 28	39	-	-	-	-	-	-
CEF-C-6458	South	3011	-	Refitted	GrA-37695	2,820 ± 30	42	-	-	-	-	-	-
					OxA18444	2,858 ± 27							
CEF-C-6459	2028	3510	6	Single	GrA-37028	2,825 ± 40	21	-	-	-	-	-	-
CEF-C-6460	2028	2117	2	Single	OxA-17872	2,459 ± 29	1589	C_{14}-C_{22}	-	-27.3	-31.7	-4.4	Ruminant dairy fats
CEF-C-6461	2028	-	-	Single	GrA-37699	2,820 ± 30	-	-	-	-	-	-	-
					OxA18445	2,815 ± 28							
CEF-C-6462	2028	2118	4	Single	GrA-35983	2,790 ± 35	-	-	-	-	-	-	-
CEF-C-6463	2028	2118	4	Single	GrA-35984	2,810 ± 35	-	-	-	-	-	-	-
CEF-C-6464	2028	2118	4	Single	GrA-35987	2,810 ± 35	350	C_{14}-C_{24}	-	-25.4	-27.1	-1.7	Mixture ruminant adipose/aquatic fats?
CEF-C-6465	2028	2119	3	Single	GrA-35988	2,830 ± 30	-	-	-	-	-	-	-
CEF-C-6466	2028	3231	2	Single	GrA-35989	2,850 ± 35	77	C_{14}-C_{18}	-	-26.7	-27.7	-1.0	Mixture ruminant adipose/aquatic fats?
CEF-C-6467	2028	3254	4	Single	GrA-35993	2,780 ± 45	237	C_{14}-C_{20}	-	-	-	-	-
CEF-C-6468	2028	3255	5	Single	GrA-35994	2,760 ± 35	8539	C_{12}-C_{26}	-	-27.2	-29.7	-2.5	Mixture ruminant adipose/aquatic fats?
CEF-C-6469	2028	3310	8	Single	GrA-35997	2,855 ± 35	474	C_{16}-C_{20}	APAAs	-26.2	-27.0	-0.8	Mixture ruminant adipose/aquatic fats
CEF-C-6470	2028	3044	8	Single	OxA-17876	2,775 ± 30	193	C_{14}-C_{18}	-	-28.1	-29.6	-1.4	Mixture ruminant adipose/aquatic fats?
CEF-C-6471	2028	3310	8	Single	OxA-17988	2,865 ± 33	238	C_{14}-C_{20}	-	-26.2	-27.9	-1.6	Mixture ruminant adipose/aquatic fats?
CEF-C-6472	2028	3232	1	Single	OxA-17915	2,778 ± 28	-	-	-	-	-	-	-
CEF-C-6473	2028	2119	3	Single	OxA-17875	2,886 ± 32	81	C_{14}-C_{20}	-	-27.1	-31.8	-4.7	Ruminant dairy fats
CEF-C-6474	2028	2118	4	Single	OxA-17873	2,773 ± 30	-	-	-	-	-	-	-
CEF-C-6475	2028	3254	4	Single	GrA-35992	3,025 ± 45	107	C_{14}-C_{20}	-	-27.5	-29.7	-2.2	Mixture ruminant adipose/aquatic fats?
					OxA-17986	3,115 ± 45							
					OxA-17987	2,860 ± 32							
CEF-C-6476	2028	2117	2		OxA-17872	2,459 ± 29	21	C_{16}-C_{20}	-	-26.8	-28.8	-1.9	Mixture ruminant adipose/aquatic fats?
CEF-C-6477	2028	2118	4	Refitted	Oxa-17873	2,773 ± 30	23	-	-	-	-	-	-
CEF-C-6478	2028	2118	4	Refitted	-	-	-	-	-	-	-	-	-
CEF-C-6479	2028	2118	4	Refitted	GrA-35987	2,810 ± 35	-	-	-	-	-	-	-

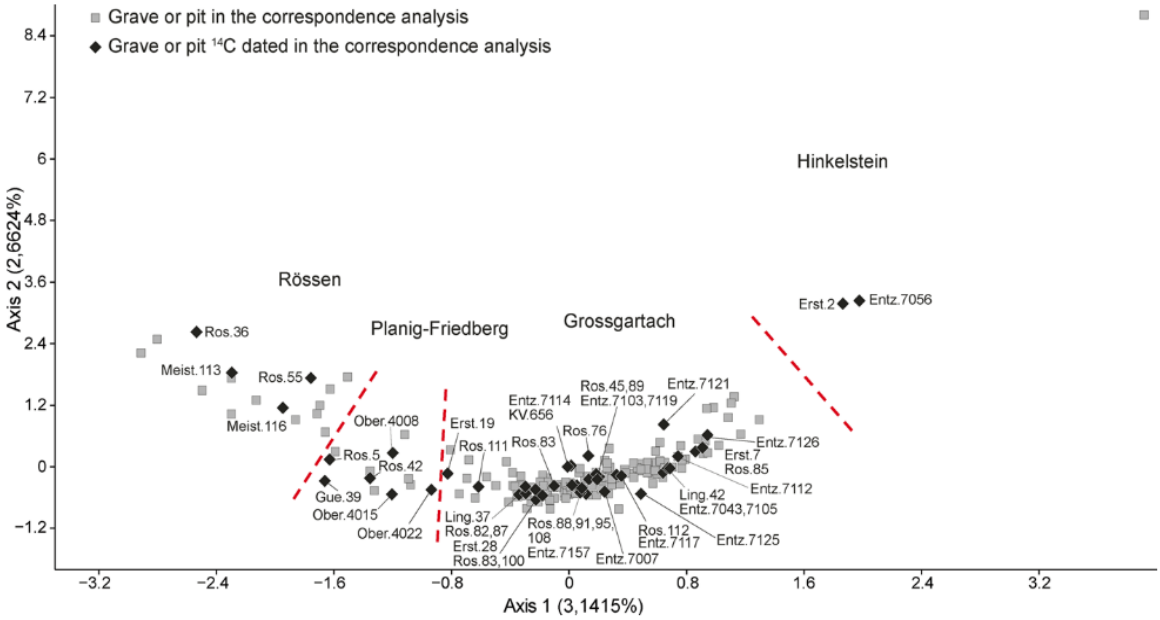
Appendix 6: Early and Middle Neolithic groups, Alsace, France

Appendix 6-1: Correspondence analysis of (a) LBK ceramics and (b) Middle Neolithic ceramics in the Lower Alsace. From Denaire *et al.* (2017, Figure 5 and Figure 10).

(a)

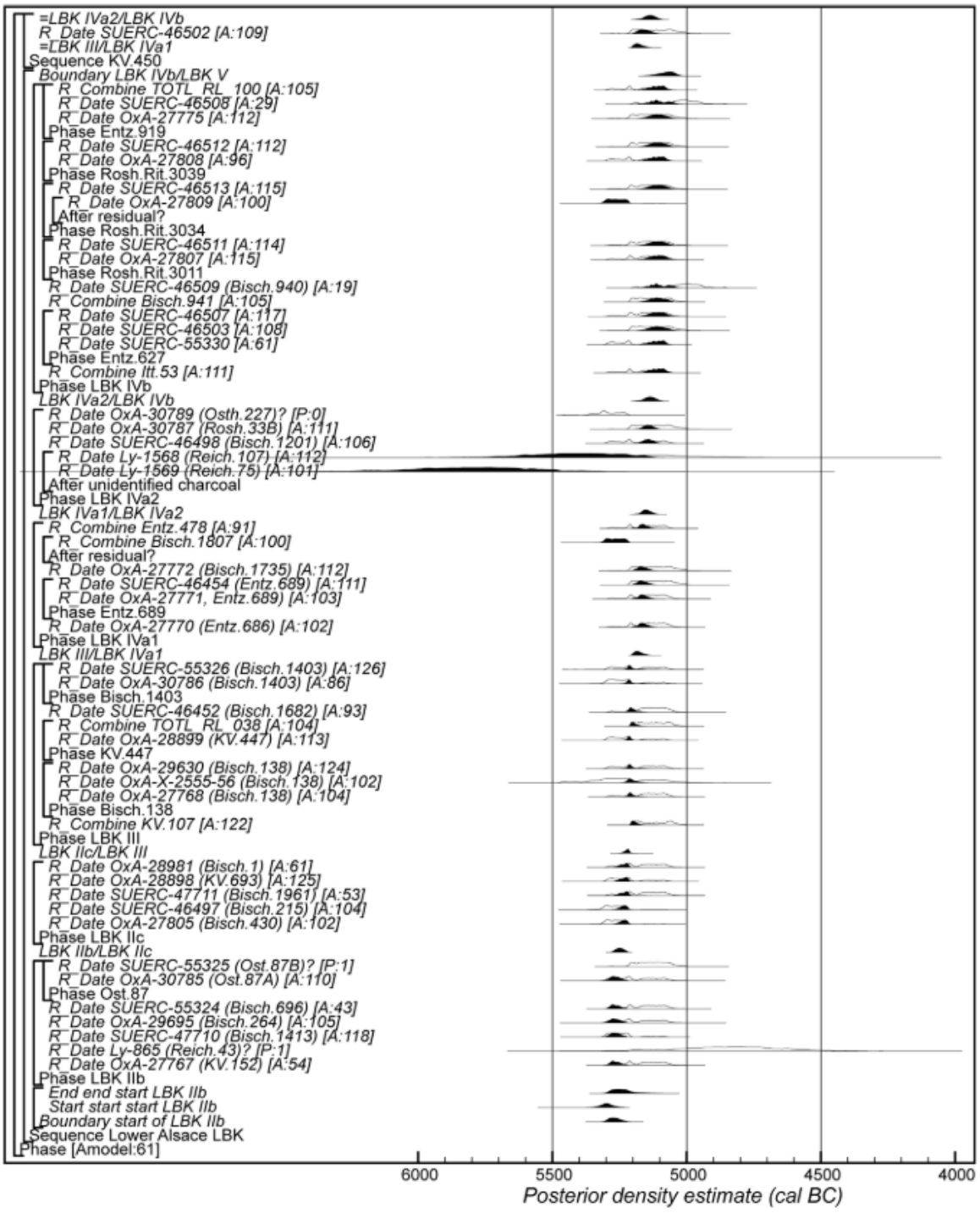


(b)

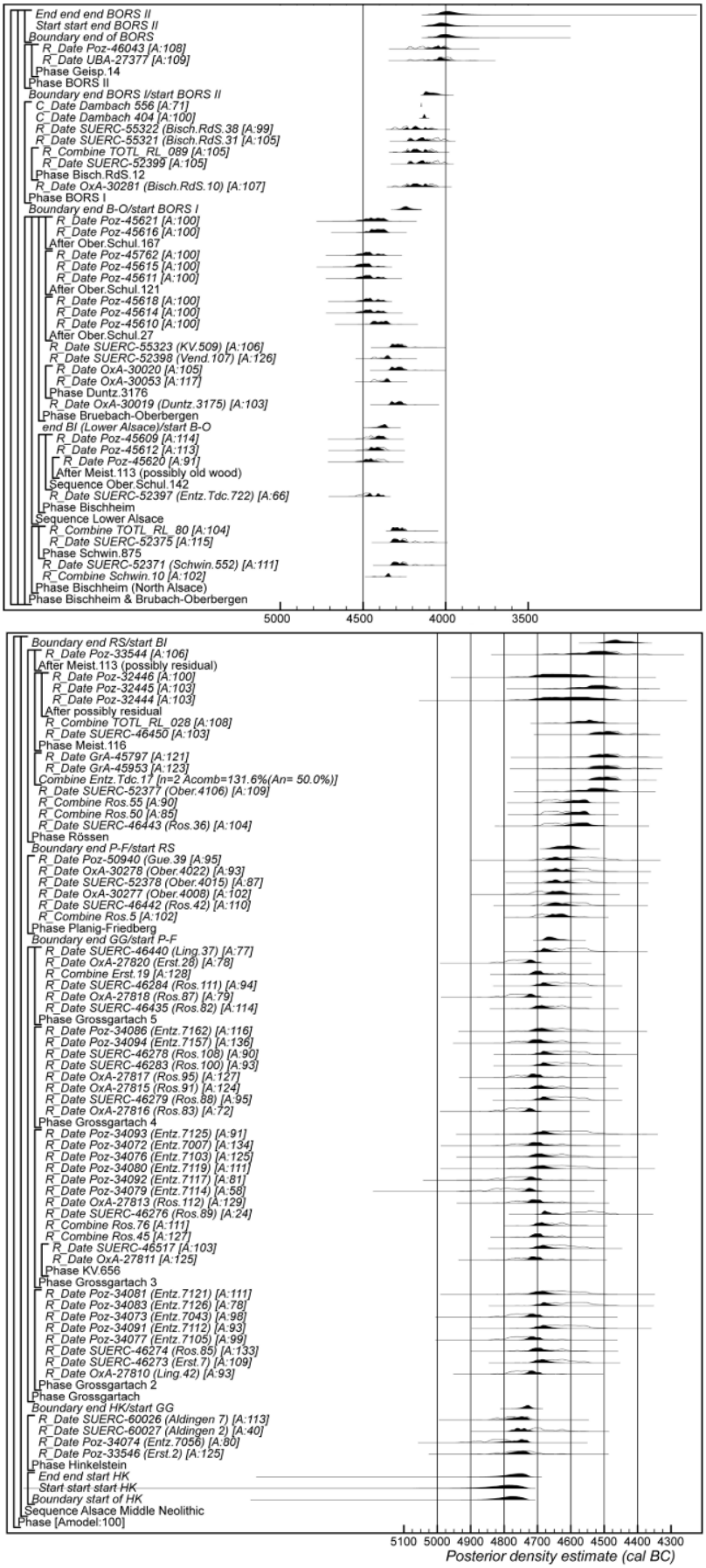


Appendix 6-2: Probability distributions of radiocarbon measurements from the sequence of (a) LBK pottery vessels (b) Middle Neolithic pottery vessels in Lower Alsace (the two figures presented are in continuity). Probability distribution plotted outlined correspond to the simple radiocarbon calibration and in black the modelled one. From Denaire *et al.* (2017, Figures 8, 15 and 16).

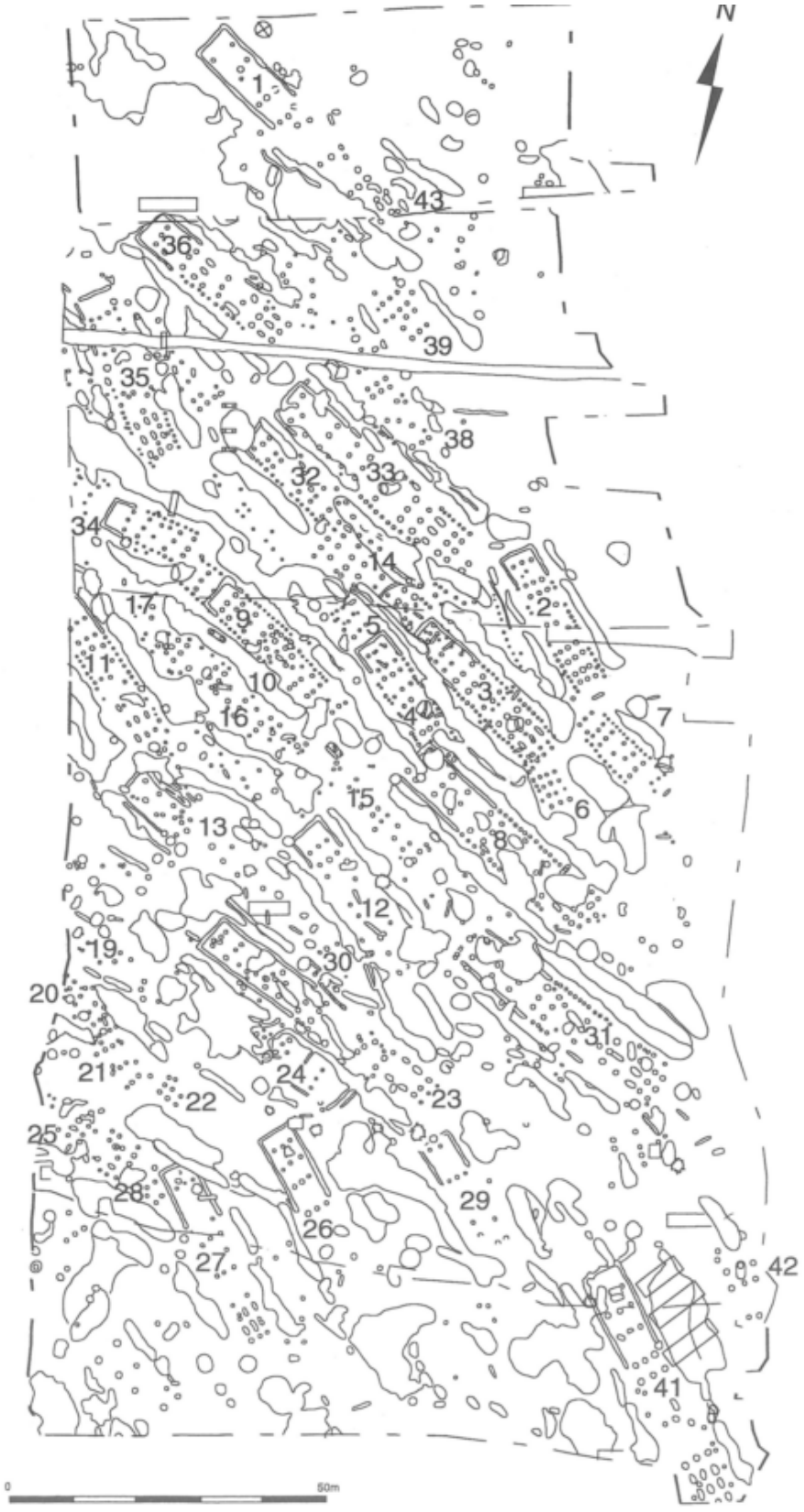
(a)



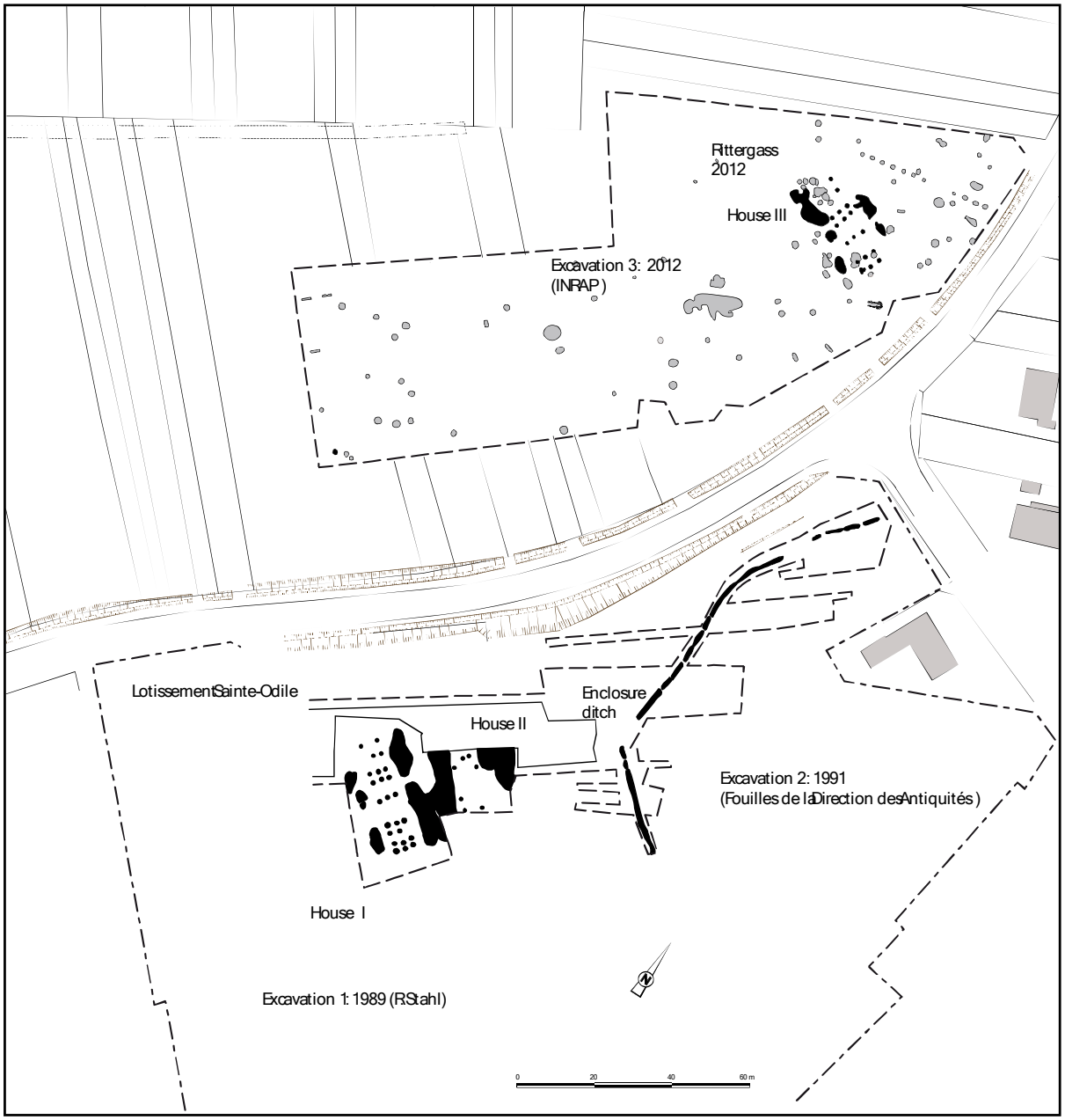
(b)


End end end BORS II
Start start end BORS II
Boundary end of BORS
R_Date Poz-46043 [A:108]
R_Date UBA-27377 [A:109]
Phase Geisp.14
Phase BORS II
Boundary end BORS I/start BORS II
C_Date Dambach 556 [A:71]
C_Date Dambach 404 [A:100]
R_Date SUERC-55322 (Bisch.RdS.38 [A:99]
R_Date SUERC-55321 (Bisch.RdS.31 [A:105]
R_Combine TOTL_RL_089 [A:105]
R_Date SUERC-52399 [A:105]
Phase Bisch.RdS.12
R_Date OxA-30281 (Bisch.RdS.10) [A:107]
Phase BORS I
Boundary end B-O/start BORS I
R_Date Poz-45621 [A:100]
R_Date Poz-45616 [A:100]
After Ober.Schul.167
R_Date Poz-45762 [A:100]
R_Date Poz-45615 [A:100]
R_Date Poz-45611 [A:100]
After Ober.Schul.121
R_Date Poz-45618 [A:100]
R_Date Poz-45614 [A:100]
R_Date Poz-45610 [A:100]
After Ober.Schul.27
R_Date SUERC-55323 (KV.509) [A:106]
R_Date SUERC-52398 (Vend.107) [A:126]
R_Date OxA-30020 [A:105]
R_Date OxA-30053 [A:117]
Phase Duntz.3176
R_Date OxA-30019 (Duntz.3175) [A:103]
Phase Bruebach-Oberbergen
end BI (Lower Alsace)/start B-O
R_Date Poz-45609 [A:114]
R_Date Poz-45612 [A:113]
R_Date Poz-45620 [A:91]
After Meist.113 (possibly old wood)
Sequence Ober.Schul.142
R_Date SUERC-52397 (Entz.Tdc.722) [A:66]
Phase Bischheim
Sequence Lower Alsace
R_Combine TOTL_RL_80 [A:104]
R_Date SUERC-52375 [A:115]
Phase Schwin.875
R_Date SUERC-52371 (Schwin.552) [A:111]
R_Combine Schwin.10 [A:102]
Phase Bischheim (North Alsace)
Phase Bischheim & Brubach-Oberbergen
5000
4500
4000
3500
Boundary end RS/start BI
R_Date Poz-33544 [A:106]
After Meist.113 (possibly residual)
R_Date Poz-32446 [A:100]
R_Date Poz-32445 [A:103]
R_Date Poz-32444 [A:103]
After possibly residual
R_Combine TOTL_RL_028 [A:108]
R_Date SUERC-46450 [A:103]
Phase Meist.116
R_Date GrA-45797 [A:121]
R_Date GrA-45953 [A:123]
Combine Entz.Tdc.17 [n=2 Acomb=131.6%(An= 50.0%)]
R_Date SUERC-52377 (Ober.4106) [A:109]
R_Combine Ros.55 [A:90]
R_Combine Ros.50 [A:85]
R_Date SUERC-46443 (Ros.36) [A:104]
Phase Rössen
Boundary end P-F/start RS
R_Date Poz-50940 (Gue.39 [A:95]
R_Date OxA-30278 (Ober.4022) [A:93]
R_Date SUERC-52378 (Ober.4015) [A:87]
R_Date OxA-30277 (Ober.4008) [A:102]
R_Date SUERC-46442 (Ros.42) [A:110]
R_Combine Ros.5 [A:102]
Phase Planig-Friedberg
Boundary end GG/start P-F
R_Date SUERC-46440 (Ling.37) [A:77]
R_Date OxA-27820 (Erst.28) [A:78]
R_Combine Erst.19 [A:128]
R_Date SUERC-46284 (Ros.111) [A:94]
R_Date OxA-27818 (Ros.87) [A:79]
R_Date SUERC-46435 (Ros.82) [A:114]
Phase Grossgartach 5
R_Date Poz-34086 (Entz.7162) [A:116]
R_Date Poz-34094 (Entz.7157) [A:136]
R_Date SUERC-46278 (Ros.108) [A:90]
R_Date SUERC-46283 (Ros.100) [A:93]
R_Date OxA-27817 (Ros.95) [A:127]
R_Date OxA-27815 (Ros.91) [A:124]
R_Date SUERC-46279 (Ros.88) [A:95]
R_Date OxA-27816 (Ros.83) [A:72]
Phase Grossgartach 4
R_Date Poz-34093 (Entz.7125) [A:91]
R_Date Poz-34072 (Entz.7007) [A:134]
R_Date Poz-34076 (Entz.7103) [A:125]
R_Date Poz-34080 (Entz.7119) [A:111]
R_Date Poz-34092 (Entz.7117) [A:81]
R_Date Poz-34079 (Entz.7114) [A:58]
R_Date OxA-27813 (Ros.112) [A:129]
R_Date SUERC-46276 (Ros.89) [A:24]
R_Combine Ros.76 [A:111]
R_Combine Ros.45 [A:127]
R_Date SUERC-46517 [A:103]
R_Date OxA-27811 [A:125]
Phase KV.656
Phase Grossgartach 3
R_Date Poz-34081 (Entz.7121) [A:111]
R_Date Poz-34083 (Entz.7126) [A:78]
R_Date Poz-34073 (Entz.7043) [A:98]
R_Date Poz-34091 (Entz.7112) [A:93]
R_Date Poz-34077 (Entz.7105) [A:99]
R_Date SUERC-46274 (Ros.85) [A:133]
R_Date SUERC-46273 (Erst.7) [A:109]
R_Date OxA-27810 (Ling.42) [A:93]
Phase Grossgartach 2
Phase Grossgartach
Boundary end HK/start GG
R_Date SUERC-60026 (Aldingen 7) [A:113]
R_Date SUERC-60027 (Aldingen 2) [A:40]
R_Date Poz-34074 (Entz.7056) [A:80]
R_Date Poz-33546 (Erst.2) [A:125]
Phase Hinkelstein
End end start HK
Start start start HK
Boundary start of HK
Sequence Alsace Middle Neolithic
Phase [Amodel:100]
5100 5000 4900 4800 4700 4600 4500 4400 4300
Posterior density estimate (cal BC)

Appendix 6-3: Site plan of Bischoffsheim “AFUA du Stade”. From Lefranc *et al.* (2004, Figures 3).



Appendix 6-4: Site plan of Rosheim “Sainte-Odile” and “Rittergass” showing the structures of early Neolithic settlements. Adapted from Lefranc and Michler (2015, Figures 2).



Appendix 6-5: Potsherds characteristics and results of lipid residue analysis at the site of Bischoffsheim. The column 'Other' corresponds to biomarkers representing the long chain ketones (K) and the beeswax esters (B), * corresponds to the distribution of both even and odd number chains for the biomarkers, its absence means only distribution odd or even-numbered compounds given by the first and last numbers, *nd* is non-determined.

Sherd #	Pit	Unit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-3991	1413	North	II C	Refitted, fine, decorated	64	C_{14}-C_{26}	C_{16}-C_{30}	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-3992	1413	A1	II	Single, fine, decorated	19	C_{16}-C_{24}	C_{16}-C_{26}	C_{27}-C_{29}	-	-	-	-	-
BIS-C-3993	1413	A3	II	Single, fine, decorated	4	-	-	-	-	-	-	-	-
BIS-C-3994	1413	A4	II	Single, coarse, undecorated	418	C_{14}-C_{24}*	-	-	-	-28.1	-30.5	-2.4	Mixture ruminant and non-ruminant adipose fats
BIS-C-3995	1413	A5	II	Single, fine, decorated	40	C_{16}-C_{20}	C_{16}-C_{26}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-3996	1413	A8	II	Refitted, fine, decorated	42	C_{16}-C_{30}	C_{16}-C_{30}	C_{25}-C_{33}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-3997	1413	A11	II	Single, fine, decorated	272	C_{16}-C_{26}	C_{18}-C_{26}	C_{27}-C_{31}	-	*nd*	*nd*	*nd*	Animal fats
BIS-C-3998	1413	A11	II	Refitted, fine, decorated	61	C_{16}-C_{18}	-	-	-	-25.4	-24.6	0.8	Non-ruminant
BIS-C-3999	1413	A11	II	Single, coarse, decorated	9	-	-	-	-	-	-	-	*nd*
BIS-C-4000	1413	A11	II	Single, fine, decorated	10	-	-	-	-	-	-	-	*nd*
BIS-C-4001	1413	B2	II	Single, fine, decorated	3	-	-	-	-	-	-	-	-
BIS-C-4002	1413	B3	II	Coarse, undecorated	50	C_{14}-C_{24}*	C_{18}	-	-	-27.5	-29.8	-2.4	Mixture ruminant and non-ruminant adipose fats
BIS-C-4003	1413	B4	II	Single, fine, decorated	16	C_{16}-C_{24}	C_{18}, C_{24}-C_{26}	-	-	-	-	-	*nd*
BIS-C-4004	1413	B5	II	Single, coarse, undecorated	44	C_{14}-C_{30}	-	-	-	-25.1	-24.8	0.3	Non-ruminant
BIS-C-4005	1961	A3	II C	Refitted, fine, decorated	49	C_{16}-C_{26}	C_{18}-C_{28}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-4006	1961	A5	II C	Refitted, fine, decorated	3	-	-	-	-	-	-	-	-
BIS-C-4007	1961	A5	II C	Single, fine, decorated	204	C_{16}-C_{24}	C_{17}-C_{28}	C_{25}-C_{31}	-	-28.3	-30.3	-2.1	Mixture ruminant and non-ruminant adipose fats
BIS-C-4008	1961	A5	II C	Refitted, fine, decorated	16	-	-	-	-	-	-	-	*nd*
BIS-C-4009	1961	A9	II C	Single, fine, decorated	139	C_{16}-C_{28}	C_{18}	-	-	-	-	-	Probably modern contamination
BIS-C-4010	1961	A12	II C	Refitted, fine, decorated	35	C_{16}-C_{30}	C_{16}-C_{32}	C_{25}-C_{31}	-	-	-	-	Plants?
BIS-C-4011	1961	B2	II C	Refitted, coarse, decorated	19	C_{16}-C_{26}	C_{16}-C_{26}	-	-	-	-	-	*nd*
BIS-C-4012	1961	B2	II C	Single, fine, decorated	19	C_{16}-C_{26}	C_{18}-C_{26}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4013	1961	B3	II C	Refitted, fine, decorated	207	C_{16}-C_{26}	C_{20}-C_{30}	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and plants/beeswax
BIS-C-4014	1961	B3	II C	Refitted, fine, decorated	9	C_{16}-C_{26}	C_{18}-C_{26}	C_{25}-C_{29}	-	-	-	-	*nd*
BIS-C-4015	1961	B3	II C	Single, fine, decorated	12	C_{16}, C_{18}	C_{18}, C_{20}	C_{29}	-	-	-	-	*nd*
BIS-C-4016	1961	B10	II C	Single, fine, decorated	10	C_{16}-C_{20}	C_{18}	-	-	-	-	-	*nd*
BIS-C-4017	1961	B12	II C	Single, fine, decorated	61	C_{15}-C_{28}*	C_{16}-C_{26}, C_{17}	-	-	-28.1	-31.1	-3.1	Mixture ruminant and non-ruminant adipose fats
BIS-C-4018	1961	B12	II C	Single, fine, decorated	107	C_{16}-C_{20}, C_{17}	C_{18}	-	-	-28.3	-28.8	-0.5	Mixture ruminant and non-ruminant adipose fats
BIS-C-4019	375	A1	III	Single, coarse, undecorated	10	-	-	-	-	-	-	-	*nd*
BIS-C-4020	375	A5	III	Single, fine, decorated	56	-	-	-	-	-	-	-	*nd*
BIS-C-4021	375	A7	III	Single, fine, decorated	41	-	-	-	-	-	-	-	Probably modern contamination
BIS-C-4022	375	A10	III	Single, fine, decorated	16	C_{16}-C_{18}	-	C_{27}	-	-	-	-	Probably modern contamination
BIS-C-4023	375	B1	III	Refitted, fine, decorated	55	C_{14}-C_{30}*	C_{16}-C_{30}	C_{25}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-4024	375	B1	III	Refitted, fine, decorated	26	C_{14}-C_{26}*	C_{18}, C_{24}-C_{26}	C_{25}-C_{33}	-	*nd*	*nd*	*nd*	Animal fats?
BIS-C-4025	375	B3	III	Single, fine, decorated	48	C_{16}-C_{28}*	-	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Animal fats?
BIS-C-4026	375	B3	III	Refitted, fine, decorated	8	-	-	-	-	-	-	-	*nd*
BIS-C-4027	375	B6	III	Single, fine, decorated	84	C_{14}-C_{26}	C_{30}	C_{23}-C_{31}	-	-	-	-	Probably modern contamination
BIS-C-4028	375	B9	III	Single, coarse, undecorated	24	C_{14}-C_{24}	C_{14}-C_{20}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4029	375	B10	III	Single, fine, decorated	64	C_{14}-C_{30}	C_{24}-C_{32}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-4030	375	B14	III	Single, fine, decorated	11	C_{14}-C_{18}, C_{24}	C_{14}-C_{24}	-	-	-	-	-	*nd*
BIS-C-4031	375	B15	III	Refitted, fine, decorated	10	C_{14}-C_{18}	C_{14}-C_{24}*	-	-	-	-	-	*nd*
BIS-C-4032	538	A13	IVa1	Single, fine, decorated	89	C_{14}-C_{26}	C_{18}.C_{20}	-	-	-	-	-	-
BIS-C-4033	538	A17	IVa1	Single, fine, decorated	11	C_{14}-C_{28}	C_{14}-C_{28}*	C_{25}-C_{31}	-	-	-	-	*nd*
BIS-C-4034	538	A22	IVa1	Single, fine, decorated	29	C_{14}-C_{30}*	C_{14}-C_{30}	C_{23}-C_{33}*	B	-	-	-	Beeswax
BIS-C-4035	538	A22	IVa1	Single, fine, decorated	22	C_{14}-C_{28}	C_{15}-C_{30}*	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4036	538	A22	IVa1	Single, coarse, undecorated	4	C_{16}-C_{26}	C_{18}-C_{28}	-	-	-	-	-	-
BIS-C-4037	538	A22	IVa1	Refitted, fine, decorated	29	C_{14}-C_{30}	C_{14}-C_{30}	C_{23}-C_{31}	B	-	-	-	Beeswax
BIS-C-4038	538	A23	IVa1	Single, fine, decorated	149	C_{16}-C_{34}	C_{18}-C_{34}	C_{23}-C_{31}	B	-	-	-	Beeswax

Sherd #	Pit	Unit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-4039	538	A24	IVa1	Single, fine, decorated	12	C_{15}, C_{16}-C_{24}	C_{16}-C_{24}	-	-	-	-	-	*nd*
BIS-C-4040	538	B3	IVa1	Single, fine, decorated	13	C_{16}-C_{18}, C_{24}	C_{15}, C_{16}-C_{18}	-	-	-	-	-	Probably modern contamination
BIS-C-4041	538	B23	IVa1	Single, fine, decorated	7	C_{16}-C_{24}	C_{18}-C_{26}	-	-	-	-	-	*nd*
BIS-C-4042	538	B24	IVa1	Single, fine, decorated	12	C_{16}-C_{18}	C_{16}-C_{22}	-	-	-	-	-	*nd*
BIS-C-4043	538	B24	IVa1	Single, fine, decorated	62	C_{16}-C_{28}, C_{17}	C_{16}-C_{30}	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-4044	538	B25	IVa1	Single, fine, decorated	72	C_{14}-C_{30}, C_{17}	C_{14}-C_{32}	C_{23}-C_{33}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-4045	538	B31	IVa1	Single, fine, decorated	15	-	C_{18}	-	-	-	-	-	Probably modern contamination
BIS-C-4046	538	B36	IVa1	Single, fine, decorated	20	C_{16}-C_{28}	C_{16}-C_{28}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4047	265	A3	IVa2	Single, fine, decorated	48	C_{14}-C_{24}	C_{14}-C_{18}	-	-	-26.0	-26.5	-0.6	Mixture ruminant and non-ruminant adipose fats
BIS-C-4048	265	A4	IVa2	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4049	265	A4	IVa2	Single, fine, decorated	15	C_{16}-C_{26}	C_{18}-C_{20}	-	-	-	-	-	*nd*
BIS-C-4050	265	A5	IVa2	Single, fine, decorated	5	-	-	-	-	-	-	-	-
BIS-C-4051	265	A5	IVa2	Single, fine, decorated	1	-	-	-	-	-	-	-	-
BIS-C-4052	265	A5	IVa2	Single, coarse, undecorated	7	-	-	-	-	-	-	-	*nd*
BIS-C-4053	265	A6	IVa2	Refitted, coarse, undecorated	31	C_{16}-C_{18}	C_{14}-C_{24}	-	-	-	-	-	*nd*
BIS-C-4054	265	A6	IVa2	Single, fine, decorated	83	C_{16}-C_{30}	C_{16}-C_{30}	C_{21}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-4055	265	A7	IVa2	Single, fine, decorated	39	C_{16}-C_{28}	C_{16}-C_{28}	C_{23}, C_{29}	-	-	-	-	Probably modern contamination
BIS-C-4056	265	A8	IVa2	Refitted, fine, decorated	67	C_{16}-C_{28}	C_{18}-C_{30}	C_{25}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and plants/beeswax
BIS-C-4057	265	B1	IVa2	Single, fine, decorated	88	C_{16}-C_{28}	C_{16}-C_{32}	C_{23}-C_{31}	-	-	-	-	Plants?
BIS-C-4058	265	B8	IVa2	Refitted, fine, decorated	63	C_{16}-C_{30}	C_{16}-C_{30}	C_{23}-C_{33}	-	*nd*	*nd*	*nd*	Mixture animal fats and plants?
BIS-C-4059	265	B8	IVa2	Refitted, fine, decorated	74	C_{12}-C_{28}, C_{17}	C_{10}-C_{30}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and plants?
BIS-C-4060	265	B8	IVa2	Single, fine, decorated	63	C_{16}-C_{26}	C_{15}-C_{30}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-4061	941	A14	IVb	Single, fine, decorated	318	C_{14}-C_{28}	C_{12}-C_{30}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture ruminant and non-ruminant adipose fats
BIS-C-4062	941	A14	IVb	Refitted, fine, decorated	36	C_{14}-C_{29}	C_{14}-C_{28}*	C_{21}-C_{31}	-	-	-	-	*nd*
BIS-C-4063	941	A14	IVb	Single, coarse, undecorated	6518	C_{14}-C_{22}	-	-	-	-25.1	-25.5	-0.4	Ruminant fats
BIS-C-4064	941	A14	IVb	Single, coarse, decorated	53	C_{14}-C_{30}	C_{14}-C_{30}	C_{23}-C_{31}	-	-	-	-	Plants?
BIS-C-4065	941	A14	IVb	Single, coarse, undecorated	19	C_{14}-C_{28}	C_{14}-C_{26}	-	-	-	-	-	*nd*
BIS-C-4066	941	A14	IVb	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4067	941	B13	IVb	Single, fine, decorated	75	C_{14}-C_{28}	C_{14}-C_{28}*	C_{25}-C_{31}	-	-	-	-	*nd*
BIS-C-4068	941	B15	IVb	Single, fine, decorated	121	C_{14}-C_{28}*	C_{16}-C_{32}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and plants?
BIS-C-4069	941	B15	IVb	Single, fine, decorated	43	C_{14}-C_{30}*	C_{14}-C_{28}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4070	941	C5	IVb	Single, fine, decorated	40	C_{14}-C_{28}	-	C_{27}-C_{31}	-	-	-	-	*nd*
BIS-C-4071	941	C7	IVb	Single, fine, decorated	85	C_{14}-C_{18}	C_{12}-C_{24}	-	-	-	-	-	*nd*
BIS-C-4501	375	A1	III	Single, coarse, undecorated	515	C_{14}-C_{24}, C_{17}	C_{12}-C_{18}	-	-	-26.0	-26.6	-0.6	Mixture ruminant and non-ruminant adipose fats
BIS-C-4502	375	A1	III	Single, coarse, undecorated	55	C_{14}-C_{28}*	C_{16}-C_{30}	C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-4503	375	A3	III	Single, coarse, undecorated	585	C_{14}-C_{26}	C_{12}-C_{18}	-	-	-26.3	-26.9	-0.7	Mixture ruminant and non-ruminant adipose fats
BIS-C-4504	375	A3	III	Single, coarse, undecorated	1490	C_{14}-C_{24}	C_{16}-C_{20}	C_{25}, C_{27}	-	-26.9	-28.3	-1.4	Mixture ruminant and non-ruminant fats
BIS-C-4505	375	A3	III	Single, coarse, undecorated	1002	C_{14}-C_{20}	C_{12}-C_{30}	-	-	-26.1	-26.8	-0.6	Mixture ruminant and non-ruminant fats
BIS-C-4506	375	A7	III	Single, coarse, undecorated	54	C_{14}-C_{24}	C_{12}-C_{20}	-	-	-	-	-	*nd*
BIS-C-4507	375	B2	III	Single, coarse, undecorated	651	$C1_4$-C_{28}	C_{16}-C_{26}	-	-	-27.3	-28.4	-1.1	Mixture ruminant and non-ruminant adipose fats
BIS-C-4508	375	B2	III	Single, coarse, undecorated	535	C_{14}-C_{26}	C_{14}-C_{18}, C_{17}	-	-	-25.7	-26.4	-0.8	Mixture ruminant and non-ruminant adipose fats
BIS-C-4509	375	B3	III	Single, coarse, undecorated	74	C_{14}-C_{30}	C_{14}-C_{30}	C_{23}-C_{31}	-	-	-	-	
BIS-C-4510	375	B4	III	Single, coarse, undecorated	5	C_{14}-C_{28}	C_{16}-C_{26}	C_{23}-C_{27}	-	-	-	-	-
BIS-C-4511	375	B5	III	Single, coarse, undecorated	167	C_{14}-C_{22}	C_{14}-C_{18}	-	-	-26.3	-26.3	0.0	Mixture ruminant and non-ruminant adipose fats
BIS-C-4512	375	B6	III	Single, coarse, undecorated	3	C_{14}-C_{26}	C_{14}-C_{26}	-	-	-	-	-	-
BIS-C-4513	375	B10	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-4514	375	B11	III	Single, coarse, undecorated	1015	C_{14}-C_{28}, C_{17}	C_{14}-C_{32}	C_{23}-C_{31}	-	-27.6	-31.4	-3.8	Mixture dairy and non-ruminant adipose fats?
BIS-C-4515	375	B11	III	Single, coarse, undecorated	376	C_{14}-C_{26}	-	-	-	-28.8	-30.1	-1.3	Mixture ruminant and non-ruminant adipose fats
BIS-C-4516	375	B12	III	Single, fine, decorated	0	-	-	-	-	-	-	-	-
BIS-C-4517	538	A16	IVa1	Single, coarse, undecorated	13	C_{14}-C_{18}	C_{14}-C_{20}	-	-	-	-	-	*nd*
BIS-C-4518	538	A16	IVa1	Single, coarse, undecorated	4329	C_{14}-C_{26}	C_{17},C_{18},C_{19}	-	-	-30.5	-32.8	-2.3	Ruminant adipose fats
BIS-C-4519	538	A17	IVa1	Single, coarse, undecorated	1434	C_{14}-C_{20}	C_{12}-C_{18}	-	-	-24.5	-23.6	0.9	Non-ruminant adipose fats
BIS-C-4520	538	A23	IVa1	Single, coarse, undecorated	81	C_{14}-C_{24}	C_{12}-C_{20}	-	-	-30.0	-32.3	-2.3	Ruminant adipose fats

Sherd #	Pit	Unit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-4521	538	A24	IVa1	Single, coarse, undecorated	166	C_{14}-C_{24}	C_{14}-C_{20}	-	-	-30.3	-32.5	-2.2	Ruminant adipose fats
BIS-C-4522	538	A24	IVa1	Refitted, coarse, undecorated	668	C_{14}-C_{22}	C_{18}	-	-	-30.8	-32.4	-1.7	Ruminant adipose fats
BIS-C-4523	538	A24	IVa1	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-4524	538	A24	IVa1	Single, coarse, undecorated	131	C_{14}-C_{26}, C_{17}	C_{16}-C_{18}	-	-	-27.9	-30.0	-2.1	Mixture ruminant and non-ruminant adipose fats
BIS-C-4525	538	A25	IVa1	Single, coarse, undecorated	78	C_{14}-C_{26}*	C_{14}-C_{18}	-	-	-25.4	-24.6	0.9	-
BIS-C-4526	538	A25	IVa1	Single, coarse, undecorated	3	C_{14}-C_{26}	C_{14}-C_{18}	C_{21}-C_{27}	-	-	-	-	-
BIS-C-4527	538	A36	IVa1	Single, coarse, undecorated	2477	C_{14}-C_{24}, C_{17}	C_{14}-C_{18}	-	-	-30.9	-35.0	-4.1	Dairy fats
BIS-C-4528	538	A36	IVa1	Single, coarse, undecorated	580	C_{14}-C_{24}*	C_{14}-C_{18}	-	-	-30.3	-34.1	-3.8	Dairy fats
BIS-C-4529	538	B3	IVa1	Single, coarse, undecorated	2021	C_{14}-C_{22}	-	-	-	-25.9	-26.6	-0.7	Mixture ruminant and non-ruminant fats
BIS-C-4530	538	B23	IVa1	Single, coarse, undecorated	19	C_{14}-C_{30}	C_{16}-C_{30}	C_{23}-C_{31}	B	-	-	-	Mixture animal fats and beeswax?
BIS-C-4531	538	B23	IVa1	Single, coarse, undecorated	973	C_{14}-C_{24}, C_{17}	-	-	-	-24.9	-24.6	0.3	Non-ruminant adipose fats
BIS-C-4532	538	B24	IVa1	Single, coarse, undecorated	7	C_{16}-C_{28}, C_{17}	C_{18}-C_{30}	C_{21}-C_{31}	-	-	-	-	*nd*
BIS-C-4533	538	B24	IVa1	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-4534	538	B25	IVa1	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-4535	538	B25	IVa1	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4536	538	B25	IVa1	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-4537	538	B28	IVa1	Single, coarse, undecorated	609	C_{14}-C_{24}, C_{17}	C_{14}-C_{18}	-	-	-23.8	-23.6	0.2	Non-ruminant
BIS-C-4538	538	D25	IVa1	Single, coarse, undecorated	190	C_{14}-C_{26}, C_{17}	C_{14}-C_{18}	-	-	-25.5	-26.5	-1.1	Mixture ruminant and non-ruminant adipose fats
BIS-C-4539	538	D25	IVa1	Single, coarse, undecorated	126	C_{12}-C_{24}*	C_{12}-C_{18}	-	-	-26.2	-26.5	-0.2	Mixture ruminant and non-ruminant adipose fats
BIS-C-4540	265	A2	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4541	265	A2	IVa2	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4542	265	A3	IVa2	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
BIS-C-4543	265	A3	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4544	265	A3	IVa2	Single, coarse, undecorated	162	C_{14}-C_{26}*	-	-	-	-27.2	-31.1	-3.9	Mixture dairy, non-ruminant adipose fats
BIS-C-4545	265	A5	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4546	265	A5	IVa2	Single, coarse, undecorated	1395	C_{13}-C_{20}*	-	-	-	-26.8	-28.8	-2.0	Mixture ruminant, non-ruminant adipose fats
BIS-C-4547	265	A5	IVa2	Single, coarse, undecorated	0	-	-	1.00	-	-	-	-	-
BIS-C-4548	265	A5	IVa2	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4549	265	A6	IVa2	Single, coarse, undecorated	806	C_{12}-C_{20}*	-	-	-	-27.0	-28.7	-1.8	Mixture ruminant and non-ruminant adipose fats
BIS-C-4550	265	A6	IVa2	Single, coarse, undecorated	267	C_{14}-C_{20}*	C_{18}	-	-	-27.5	-28.7	-1.3	Mixture ruminant and non-ruminant adipose fats
BIS-C-4551	265	A13	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4552	265	A13	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4553	265	A13	IVa2	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
BIS-C-4554	265	B3	IVa2	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4555	265	B8	IVa2	Single, coarse, undecorated	22	C_{14}-C_{18}	C_{12}-C_{22}	-	-	-	-	-	*nd*
BIS-C-4556	941	A8	IVb	Single, coarse, undecorated	91	C_{14}-C_{24}	C_{14}-C_{18}	-	-	-29.5	-30.3	-0.9	Ruminant adipose fats
BIS-C-4557	941	A8	IVb	Single, coarse, undecorated	16	C_{16}-C_{20}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-4558	941	A10	IVb	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-4559	941	A18	IVb	Single, coarse, undecorated	328	C_{14}-C_{24}*	C_{16}, C_{18}	-	-	-26.3	-28.4	-2.0	Mixture ruminant and non-ruminant adipose fats
BIS-C-4560	941	B5	IVb	Single, coarse, undecorated	589	C_{14}-C_{26}*	C_{16}	-	-	-26.3	-26.9	-0.6	Mixture ruminant and non-ruminant adipose fats
BIS-C-4561	941	B5	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4562	941	B7	IVb	Single, coarse, undecorated	9	C_{16}-C_{24}	C_{18}	-	-	-	-	-	*nd*
BIS-C-4563	941	B17	IVb	Single, fine, undecorated	146	C_{12}-C_{26}	C_{14}-C_{28}	-	-	-	-	-	Mixture animal fats and plants?
BIS-C-4564	941	B17	IVb	Single, coarse, undecorated	9	C_{14}-C_{22}	C_{18}	-	-	-27.3	-29.6	-2.3	Mixture ruminant and non-ruminant adipose fats
BIS-C-4565	941	B19	IVb	Single, coarse, undecorated	46	C_{14}-C_{26}	C_{16}-C_{30}	-	B	-	-	-	Beeswax
BIS-C-4566	941	C5	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4567	941	C5	IVb	Single, coarse, undecorated	1475	C_{14}-C_{20}	C_{14}	-	-	-27.8	-27.8	0.0	Mixture ruminant and non-ruminant adipose fats
BIS-C-4568	941	C5	IVb	Single, coarse, undecorated	1227	C_{14}-C_{20}	C_{12}-C_{16}	-	K	-27.4	-27.3	0.2	Mixture ruminant and non-ruminant adipose fats
BIS-C-4569	941	C5	IVb	Single, coarse, undecorated	152	C_{14}-C_{24}	C_{14}-C_{20}	-	-	-27.5	-30.0	-2.4	Mixture ruminant and non-ruminant adipose fats
BIS-C-4570	941	C5	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4571	941	C5	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-4572	941	C5	IVb	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
BIS-C-4573	941	C7	IVb	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-

Sherd #	Pit	Unit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-4574	941	C7	IVb	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
BIS-C-4575	941	C7	IVb	Single, coarse, undecorated	8	C_{16}-C_{20}	C_{18}	-	-	-	-	-	*nd*
BIS-C-4576	941	C15	IVb	Single, coarse, undecorated	12	C_{14}-C_{20}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-4577	941	C21	IVb	Single, coarse, undecorated	75	C_{14}-C_{26}	C_{12}-C_{28}	-	-	-26.0	-27.3	-1.3	Mixture ruminant and non-ruminant adipose fats
BIS-C-4578	941	C21	IVb	Single, coarse, undecorated	28	C_{14}-C_{18}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5201	1193	A3	II B	Single, coarse, undecorated	101	C_{14}-C_{26}*	C_{16}-C_{18}	-	-	-25.6	-26.3	-0.6	Mixture ruminant and non-ruminant adipose fats
BIS-C-5202	1193	A3	II B	Single, coarse, undecorated	52	C_{14}-C_{26}*	C_{14}-C_{19}*	-	-	-28.8	-31.2	-2.4	Ruminant adipose fats
BIS-C-5203	1193	A4	II B	Single, fine, undecorated	459	C_{14}-C_{18}, C_{17}	-	-	-	-28.7	-30.8	-2.1	Ruminant adipose fats
BIS-C-5204	1193	South	II B	Single, coarse, undecorated	241	C_{16}-C_{18}*	-	-	-	-28.9	-31.3	-2.4	Ruminant adipose fats
BIS-C-5205	1193	South	II B	Single, coarse, undecorated	15	C_{16}-C_{18}	C_{16}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5206	1193	South	II B	Single, coarse, undecorated	10	-	-	-	-	-	-	-	*nd*
BIS-C-5207	1193	South	II B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-5208	1193	South	II B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-5209	1193	South	II B	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
BIS-C-5210	1193	South	II B	Single, coarse, undecorated	193	C_{14}-C_{28}*	C_{14}-C_{18}	-	-	-27.4	-30.6	-3.2	Mixture ruminant and non-ruminant adipose fats
BIS-C-5211	1927	A3	II C	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
BIS-C-5212	1927	A3	II C	Single, coarse, undecorated	71	C_{16}-C_{28}*	C_{16}, C_{18}	-	-	-24.5	-24.7	-0.2	Ruminant fats
BIS-C-5213	1927	A4	II C	Single, coarse, undecorated	65	C_{14}-C_{18}	-	-	-	-27.5	-29.8	-2.3	Mixture ruminant and non-ruminant adipose fats
BIS-C-5214	1927	B5/6/7	II C	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5215	1927	B5/6/7	II C	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
BIS-C-5216	1927	B5/6/7	II C	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5217	1927	B5/6/7	II C	Single, fine, undecorated	11	-	-	-	-	-	-	-	*nd*
BIS-C-5218	1927	B5/6/7	II C	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5219	1927	B10	II C	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5220	1927	B10	II C	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
BIS-C-5221	264	A11	II B	Single, coarse, undecorated	22	C_{14}-C_{26}*	C_{14}-C_{20}	-	-	-	-	-	*nd*
BIS-C-5222	264	A12	II B	Single, coarse, undecorated	3	C_{14}-C_{30}	C_{14}-C_{22}, C_{28}	-	-	-	-	-	-
BIS-C-5223	264	A14	II B	Single, coarse, undecorated	66	C_{14}-C_{28}*	C_{14}-C_{24}	-	-	-	-	-	*nd*
BIS-C-5224	264	A14	II B	Single, coarse, undecorated	12	C_{14}-C_{16},C_{20}-C_{26}	C_{12}-C_{18}*	-	-	-	-	-	*nd*
BIS-C-5225	264	A14	II B	Single, coarse, undecorated	12	C_{14}-C_{24}*	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5226	264	A14	II B	Single, coarse, undecorated	34	C_{14}-C_{22}*	C_{14}-C_{22}	-	-	-	-	-	*nd*
BIS-C-5227	264	A15	II B	Single, coarse, undecorated	48	C_{14}-C_{18}	C_{12}-C_{20}	-	-	-	-	-	*nd*
BIS-C-5228	264	A15	II B	Single, coarse, undecorated	6	C_{14}-C_{30}	C_{12}-C_{26}	-	-	-	-	-	*nd*
BIS-C-5229	264	A16	II B	Single, coarse, undecorated	21	C_{14}-C_{24}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5230	264	B13	II B	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
BIS-C-5231	264	B13	II B	Single, coarse, undecorated	6	C_{12}-C_{26}	C_{12}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5232	264	B13	II B	Single, coarse, undecorated	7	C_{14}-C_{26}*	C_{16}, C_{18}	-	-	-	-	-	*nd*
BIS-C-5233	264	B14	II B	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5234	264	B14	II B	Single, coarse, undecorated	16	C_{14}-C_{26}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5235	264	B14	II B	Single, coarse, undecorated	48	C_{14}-C_{24}	C_{14}-C_{20}	-	-	-	-	-	*nd*
BIS-C-5236	264	B14	II B	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5237	264	B15	II B	Single, coarse, undecorated	18	C_{14}-C_{26}	C_{18}	-	-	-30.0	-29.8	0.3	Non-ruminant adipose fats
BIS-C-5238	264	B17	II B	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
BIS-C-5239	138	A11	III	Single, coarse, undecorated	793	C_{14}-C_{26}*	C_{18}	-	-	-28.4	-30.4	-2.0	Ruminant adipose fats
BIS-C-5240	138	A20	III	Single, coarse, undecorated	229	C_{16}-C_{26}	-	-	B	-	-	-	Beeswax
BIS-C-5241	138	A20	III	Single, coarse, undecorated	6	C_{16}-C_{26}	-	-	-	-	-	-	*nd*
BIS-C-5242	138	A20	III	Single, coarse, undecorated	2385	C_{14}-C_{26}*	-	-	-	-27.3	-29.3	-2.0	Mixture ruminant and non-ruminant adipose fats
BIS-C-5243	138	A20	III	Single, coarse, undecorated	531	C_{14}-C_{28}	C_{14}-C_{18}	-	-	-26.1	-27.8	-1.7	Mixture ruminant and non-ruminant adipose fats
BIS-C-5244	138	A20	III	Single, coarse, undecorated	2653	C_{14}-C_{26}*	-	-	-	-28.4	-30.4	2.0	Mixture ruminant and non-ruminant adipose fats
BIS-C-5245	138	A20	III	Single, coarse, undecorated	27	C_{16}-C_{28}	C_{22}-C_{30}	C_{25}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5246	138	A22	III	Single, coarse, undecorated	156	C_{14}-C_{30}	C_{14}-C_{32}	C_{25}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5247	138	B14	III	Single, coarse, undecorated	13	C_{14}-C_{28}*	C_{14}-C_{20}	-	-	-	-	-	*nd*
BIS-C-5248	138	B15	III	Single, coarse, undecorated	16	C_{16}-C_{28}	C_{16}-C_{26}	-	-	-	-	-	*nd*

Sherd #	Pit	Unit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-5249	138	B15	III	Single, coarse, undecorated	418	C_{14}-C_{24}	C_{14}-C_{18}	-	-	-27.2	-29.8	-2.6	Mixture ruminant and non-ruminant adipose fats
BIS-C-5250	138	B15	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
BIS-C-5251	138	B16	III	Single, coarse, undecorated	9	C_{14}-C_{24}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5252	138	B19	III	Single, coarse, undecorated	215	C_{14}-C_{28}*	C_{16}, C_{18}	-	-	-27.3	-28.1	-0.8	Mixture ruminant and non-ruminant adipose fats
BIS-C-5253	138	B20	III	Single, coarse, undecorated	19	C_{14}-C_{28}	C_{14}-C_{18}	-	-	-	-	-	Probably modern contamination
BIS-C-5254	138	B21	III	Single, coarse, undecorated	188	C_{14}-C_{30}*	-	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-5255	696	B1	II B	Single, coarse, undecorated	11	C_{16}-C_{28}*	-	-	-	-	-	-	*nd*
BIS-C-5256	696	B7	II B	Single, coarse, undecorated	12	C_{16}-C_{30}, C_{17}	C_{16}-C_{26}	-	-	-	-	-	Probably modern contamination
BIS-C-5257	696	B10	II B	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-5258	696	B10	II B	Single, coarse, undecorated	7	C_{16}, C_{18}	C_{18}	-	-	-	-	-	*nd*
BIS-C-5259	696	B11	II B	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
BIS-C-5260	696	B11	II B	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
BIS-C-5261	940	A7	IVb	Single, coarse, undecorated	10	C_{14}-C_{18}	C_{14}-C_{18}	-	-	-	-	-	*nd*
BIS-C-5262	940	A19	IVb	Single, fine, decorated	3	C_{16}-C_{26}	C_{16}, C_{18}	-	-	-	-	-	-
BIS-C-5263	940	B4	IVb	Single, coarse, undecorated	20	C_{14}-C_{28}	C_{16}, C_{19}	-	-	-	-	-	*nd*
BIS-C-5264	940	B14	IVb	Single, coarse, undecorated	158	C_{14}-C_{28}*	C_{14}-C_{30}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and plants?
BIS-C-5265	940	B18	IVb	Single, coarse, undecorated	2440	C_{14}-C_{20}	C_{14}-C_{18}	-	-	-25.7	-26.6	-0.9	Mixture ruminant and non-ruminant adipose fats
BIS-C-5266	940	C6	IVb	Single, coarse, undecorated	10	C_{14}-C_{22}	C12-C_{18}	-	-	-	-	-	*nd*
BIS-C-5267	940	D23	IVb	Single, coarse, undecorated	498	C_{14}-C_{22}	C_{18}	-	-	-25.7	-26.6	-0.9	Mixture ruminant and non-ruminant adipose fats
BIS-C-5268	940	E24	IVb	Single, coarse, undecorated	9	C_{14}-C_{18}	C_{18}	-	-	-	-	-	*nd*
BIS-C-5269	696	-	II B	Single, fine, decorated	75	C_{14}-C_{22}	C_{14}-C_{22}*	-	-	-	-	-	*nd*
BIS-C-5270	138	A13	III	Single, fine, decorated	34	C_{14}-C_{22}	C_{18}-C_{24}	-	-	-	-	-	*nd*
BIS-C-5271	138	A15	III	Single, fine, decorated	135	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-5272	138	A17	III	Single, fine, decorated	148	C_{14}-C_{26}	C_{12}-C_{28}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5273	138	A19	III	Single, fine, decorated	93	C_{14}-C_{26}	C_{12}-C_{24}	-	-	-	-	-	*nd*
BIS-C-5274	138	A20	III	Single, fine, decorated	111	C_{14}-C_{24}	C_{14}-C_{30}*	C_{27}, C_{29}	B	-	-	-	Beeswax
BIS-C-5275	138	A25	III	Single, fine, decorated	30	C_{14}-C_{22}	C_{14}-C_{21}*	-	-	-	-	-	*nd*
BIS-C-5276	138	B7	III	Single, fine, decorated	13	C_{14}-C_{18}, C_{15}	C_{16}-C_{26}	C_{25}-C_{31}	-	-	-	-	*nd*
BIS-C-5277	138	B9	III	Single, fine, decorated	102	C_{14}-C_{28}*	C_{16}-C_{30}	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Mixture animal fats and beeswax
BIS-C-5278	138	C9	III	Single, fine, decorated	35	C_{16}-C_{26}, C_{17}	C_{16}-C_{22}	-	-	-	-	-	*nd*
BIS-C-5279	264	A16	II B	Single, fine, decorated	87	C_{14}-C_{30}*	C_{12}-C_{30}	C_{20}-C_{31}*	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5280	264	B14	II B	Single, fine, decorated	11	C_{14}-C_{26}	C_{16}-C_{26}	C_{23}-C_{29}	-	-	-	-	*nd*
BIS-C-5281	264	B15	II B	Single, fine, decorated	15	C_{16}-C_{26}	C_{16}, C_{18}	-	-	-	-	-	*nd*
BIS-C-5282	264	B18	II B	Single, fine, decorated	83	C_{14}-C_{21}*	C_{14}-C_{26}, C_{17}	-	-	-	-	-	Probably modern contamination
BIS-C-5283	1201/2	F4	IVa2	Single, fine, decorated	292	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{29}*	-	-	-	-	Terrestrial C_3 plants
BIS-C-5284	1201/2	F4	IVa2	Single, fine, decorated	125	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}*	-	-	-	-	Terrestrial C_3 plants
BIS-C-5285	1201	F5	IVa2	Refitted, fine, decorated	22	C_{15}-C_{28}*	C_{14}-C_{24}	C_{23}-C_{29}	-	-	-	-	*nd*
BIS-C-5286	1201	F5	IVa2	Single, fine, decorated	346	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}*	-	-	-	-	Terrestrial C_3 plants
BIS-C-5287	1201/2	E3	IVa2	Refitted, fine, decorated	255	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}	-	-27.0	-27.9	-0.9	Mixture ruminant and non-ruminant adipose fats
BIS-C-5288	1735	B11	III	Single, fine, decorated	2058	C_{14}-C_{26}*	-	-	-	-25.6	-26.6	-0.9	Mixture ruminant and non-ruminant adipose fats
BIS-C-5289	1735	B12	III	Single, fine, decorated	66	C_{14}-C_{28}*	C_{14}-C_{26}	C_{25}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5290	430	B2	II C	Single, fine, decorated	177	C_{14}-C_{28}*	C_{16}-C_{30}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5291	430	B2	II C	Single, fine, decorated	114	C_{14}-C_{28}	C_{14}-C_{28}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5292	430	B5	II C	Single, fine, decorated	53	C_{14}-C_{28}	C_{12}-C_{20}	C_{25}-C_{29}	-	-	-	-	*nd*
BIS-C-5293	430	B5	II C	Single, fine, decorated	51	C_{14}-C_{28}	C_{14}-C_{26}	-	-	-	-	-	*nd*
BIS-C-5294	430	B5	II C	Refitted, coarse, decorated	13	C_{14}-C_{28}*	C_{14}-C_{20}	C_{23}-C_{31}	-	-	-	-	Probably modern contamination
BIS-C-5295	430	B5	II C	Single, fine, decorated	92	C_{14}-C_{28}*	C_{14}-C_{26}*	C_{23}-C_{31}	-	-	-	-	-
BIS-C-5296	940	B16	IVb	Single, fine, decorated	139	C_{14}-C_{30}*	C_{16}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
BIS-C-5297	940	B16	IVb	Single, fine, decorated	161	C_{12}-C_{30}*	C_{14}-C_{32}*	C_{23}-C_{31}	B	*nd*	*nd*	*nd*	Beeswax
BIS-C-5298	940	C6	IVb	Single, fine, decorated	37	C_{14}-C_{30}*	C_{16}, C_{18}	-	-	-	-	-	*nd*
BIS-C-5299	940	C6	IVb	Single, fine, decorated	199	C_{14}-C_{30}*	C_{16}-C_{30}	C_{23}-C_{31}	B	-	-	-	Beeswax
BIS-C-5300	1403	A1	III	Single, fine, decorated	19	C_{16}-C_{28}*, C_{15}	C_{16}-C_{24}	-	-	-	-	-	*nd*
BIS-C-5301	1403	A2	III	Single, fine, decorated	227	C_{14}-C_{26}	C_{14}-C_{26}	-	-	-28.9	-31.7	-2.8	Ruminant adipose fats

Sherd #	Pit	Unit	Phase	Description	C° (µg.g^{-1})	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BIS-C-5302	1403	B1	III	Single, fine, decorated	14	-	-	-	-	-	-	-	*nd*
BIS-C-5303	1403	B2	III	Single, fine, decorated	21	C_{14}-C_{24}*	C_{14}-C_{22}*	-	-	-	-	-	*nd*
BIS-C-5304	1403	B2	III	Single, fine, decorated	16	C_{15}, C_{16}-C_{26}	C_{14}-C_{20}*	-	-	-	-	-	*nd*
BIS-C-5305	1682	Tr 2	III	Refitted, fine, decorated	194	C_{14}-C_{26}. C_{17}	C_{14}-C_{20}	-	-	-	-	-	*nd*
BIS-C-5306	1682	B4	III	Single, fine, decorated	149	C_{14}-C_{28}	C_{14}-C_{20}*	$C2_3$-C_{31}, C_{24}	-	*nd*	*nd*	*nd*	-
BIS-C-5307	1682	B10	III	Refitted, fine, decorated	70	C_{14}-C_{26}*	C_{12}-C_{22}*	C_{25}-C_{31}	-	-	-	-	Probably modern contamination
BIS-C-5308	1807	A4	IVa1	Single, fine, decorated	1534	C_{14}-C_{30}*	C_{12}-C_{26}*	C_{23}-C_{31}, C_{24}	-	-	-	-	*nd*
BIS-C-5309	1806/7	B2	IVa1	Refitted, fine, decorated	15	-	-	-	-	-	-	-	*nd*
BIS-C-5310	1807	B4	IVa1	Single, fine, decorated	63	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5311	1807	B5	IVa1	Refitted, fine, decorated	133	C_{14}-C_{30}*	C_{14}-C_{24}	C_{23}-C_{31}	-	-	-	-	-
BIS-C-5312	1927	B6	II C	Single, fine, decorated	7	-	-	-	-	-	-	-	*nd*
BIS-C-5313	1927	B6	II C	Single, fine, decorated	420	C_{14}-C_{30}*	C_{14}-C_{30}*	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5314	215	B1	II C	Single, fine, decorated	43	C_{16}-C_{28}*	-	C_{21}-C_{31}	-	-	-	-	*nd*
BIS-C-5315	215	B7	II C	Single, fine, decorated	28	C_{14}-C_{28}	-	-	-	-	-	-	*nd*
BIS-C-5316	215	B7	II C	Single, fine, decorated	32	C_{14}-C_{28}	C_{18}	C_{20},C_{22},C_{23}-C_{31}	-	-	-	-	*nd*
BIS-C-5317	215	B11	II C	Single, fine, decorated	52	C_{14}-C_{24}, C_{15}	C_{12}-C_{18}. C_{13}	-	-	-	-	-	Probably modern contamination
BIS-C-5318	215	B11	II C	Single, fine, decorated	66	C_{14}-C_{30}*	-	C_{23}-C_{31}	-	-	-	-	-
BIS-C-5319	1927	A1	II C	Refitted, fine, decorated	72	C_{14}-C_{24}	C_{12}-C_{18}	C_{25}-C_{31}	-	-	-	-	Probably modern contamination
BIS-C-5320	1193	South	IIB	Single, fine, decorated	132	C_{14}-C_{30}*	C_{14}-C_{22}	-	-	-26.0	-25.4	0.5	Non-ruminant adipose fats
BIS-C-5321	1193	B3	II B	Single, fine, decorated	1110	C_{14}-C_{28}*	C_{18}-C_{28}	C_{23}-C_{31}	-	-29.8	-32.7	-2.8	Ruminant adipose fats
BIS-C-5322	430	B4	II C	Single, fine, decorated	27	C_{14}-C_{26}*	C_{16}-C_{26}	-	-	-	-	-	*nd*
BIS-C-5323	430	B7	II C	Single, fine, decorated	1	-	-	-	-	-	-	-	-
BIS-C-5324	430	B7	II C	Single, fine, decorated	432	C_{14}-C_{26}*	C_{12}-C_{22}*	-	K	-25.8	-25.0	0.8	Non-ruminant adipose fats
BIS-C-5325	430	B7	II C	Single, fine, decorated	289	C_{14}-C_{25}*	C_{14}-C_{18}, C_{15}	-	-	-26.1	-25.8	0.4	Non-ruminant adipose fats
BIS-C-5326	430	C1	II C	Single, fine, decorated	31	C_{14}-C_{26}*	C_{12}-C_{18}*	C_{18}	-	-	-	-	Probably modern contamination
BIS-C-5327	430	Z27	II C	Single, fine, decorated	66	C_{14}-C_{26}*	C_{14}-C_{24}*	-	-	-	-	-	*nd*
BIS-C-5328	696	B2	II B	Single, fine, decorated	28	C_{14}-C_{26}	C_{14}-C_{22}*	-	-	-	-	-	*nd*
BIS-C-5329	696	B4	II B	Single, fine, decorated	362	C_{14}-C_{30}*	C_{14}-C_{30}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax?
BIS-C-5330	696	B6	II B	Single, fine, decorated	65	C_{16}-C_{26}*	C_{16}-C_{24}	C_{23}-C_{29}	-	-	-	-	Probably modern contamination
BIS-C-5331	696	B10	II B	Single, fine, decorated	39	C_{14}-C_{28}	C_{12}-C_{26}	-	-	-	-	-	*nd*

Appendix 6-6: Potsherds characteristics and results of ORA at the site of Rosheim “Sainte-Odile and Rittergass”. The codes are analogous to those given in Appendix 6.5.

Sherd #	Pit	Phase	Description	C° (µg.g^{-1})	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ROS-C-2141	18	V	Refitted, fine, decorated	80	C_{14}-C_{17}*	-	C_{23}	-	-	-	-	Probably modern contamination
ROS-C-2142	18	V	Single, fine, undecorated	4	-	-	-	-	-	-	-	-
ROS-C-2143	18	V	Single, coarse, undecorated	706	C_{15}-C_{20}*	C_{18}	-	-	-26.2	-27.7	-1.5	Mixture ruminant and non-ruminant adipose fats
ROS-C-2144	18	V	Single, coarse, undecorated	26	C_{16}-$C2_8$	C_{18}-C_{30}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-2145	13	IVa	Single, coarse, undecorated	25	C_{16}-C_{24}	-	-	-	-26.6	-25.5	1.1	Non-ruminant adipose fats
ROS-C-2146	13	IVa	Single, coarse, undecorated	39	C_{16}-C_{20}	C_{20}-C_{24}	C_{23}-C_{27}	-	-	-	-	*nd*
ROS-C-2147	19	IVb	Refitted, fine, decorated	104	C_{14}-C_{24}*	C_{16}-C_{23}*	C_{27}	-	-	-	-	Mixture animal fats and plants
ROS-C-2148	322	V	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ROS-C-2149	322	V	Single, coarse, undecorated	93	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-2150	322	V	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2151	322	V	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2152	115	V	Single, fine, decorated	0	-	-	-	-	-	-	-	-
ROS-C-2153	115	V	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ROS-C-2154	115	V	Single, coarse, undecorated	207	C_{16}-C_{20}*	-	-	-	-26.2	-28.2	-2.0	Mixture ruminant and non-ruminant adipose fats
ROS-C-2155	28	IVa	Single, fine, undecorated	790	C_{16}-C_{22}*	C_{16}-C_{20}	-	-	-25.9	-25.4	0.5	Non-ruminant fats
ROS-C-2156	28	IVa	Single, coarse, undecorated	230	C_{15}-C_{20}*	-	-	-	-27.4	-28.8	-1.4	Mixture ruminant and non-ruminant adipose fats
ROS-C-2157	28	IVa	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
ROS-C-2158	28	IVa	Single, coarse, undecorated	272	C_{14}-C_{20}*	-	-	-	-24.5	-23.5	1.0	Non-ruminant adipose fats
ROS-C-2159	28	IVa	Single, coarse, undecorated	6	-	-	-	-	-	-	-	*nd*
ROS-C-2160	28	IVa	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ROS-C-2161	28	IVa	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2162	28	IVa	Single, fine, decorated	12	C_{16}-C_{18}	-	-	-	-	-	-	*nd*
ROS-C-2163	28	IVa	Single, fine, decorated	18	C_{14}-C_{24}, C_{15}-C_{19}	C_{18}-C_{24}	C_{23}-C_{29}	-	-	-	-	Mixture animal fats and plants?
ROS-C-2164	28	IVa	Refitted, fine, decorated	1	-	-	-	-	-	-	-	-
ROS-C-2165	28	IVa	Single, fine, decorated	1	-	-	-	-	-	-	-	-
ROS-C-2166	28	IVa	Single, fine, undecorated	2	-	-	-	-	-	-	-	-
ROS-C-2167	28	IVa	Single, coarse, undecorated	9	C_{18}	C_{20}-C_{24}	-	-	-	-	-	Probably modern contamination
ROS-C-2168	28	IVa	Single, coarse, undecorated	1413	C_{14}-C_{20}, C_{17}	-	-	-	-24.5	-25.2	-0.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-2169	33	IVa	Refitted, coarse, undecorated	2	-	-	-	-	-	-	-	-
ROS-C-2170	33	IVa	Single, fine, undecorated	132	C_{16}-C_{24}*, C_{26}-C_{30}	C_{18}-C_{30}, C_{19}	C_{27}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
ROS-C-2171	33	IVa	Single, coarse, undecorated	320	C_{16}-C_{24}*	C_{16}-C_{26}	-	-	-26.6	-27.9	-1.4	-
ROS-C-2172	33a	IVa	Refitted, fine, decorated	75	C_{14}-C_{18}*, C_{20}-C_{28}	C_{16}-C_{32}	C_{25}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
ROS-C-2173	33ab	IVa	Single, fine, decorated	12	C_{16}-C_{20}	-	-	-	-	-	-	Probably modern contamination
ROS-C-2174	33a	IVa	Single, fine, decorated	124	C_{14}-C_{18}*, C_{20}-C_{28}	C_{16}-C_{30}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
ROS-C-2175	33b	IVa	Single, coarse, undecorated	30	C_{16}-C_{24}	C_{16}-C_{18}	-	-	-25.4	-26.5	-1.2	Mixture ruminant and non-ruminant adipose fats
ROS-C-2176	33	IVa	Single, coarse, undecorated	12	C_{16}-C_{18}*	-	-	-	-	-	-	Probably modern contamination
ROS-C-2177	33c	IVa	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2178	33b	IVa	Single, fine, decorated	7	-	-	-	-	-	-	-	*nd*
ROS-C-2179	33	IVa	Single, fine, undecorated	864	C_{16}-C_{24}*	-	-	-	-27.2	-27.4	-0.2	Mixture ruminant and non-ruminant adipose fats
ROS-C-2180	33	IVa	Single, coarse, undecorated	369	C_{16}-C_{20}, C_{17}	-	-	-	-24.5	-25.1	-0.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-2181	85	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2182	85	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2183	85	IVb	Single, coarse, undecorated	194	C_{16}-C_{18}*	-	-	-	-25.7	-25.0	0.7	Non-ruminant adipose fats
ROS-C-2184	85	IVb	Single, fine, decorated	32	C_{14}-C_{24}	C_{14}-C_{22}*	C_{25}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
ROS-C-2185	320	IVb	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
ROS-C-2186	320	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2187	320	IVb	Single, coarse, undecorated	189	C_{16}-C_{24}	-	-	-	-24.5	-24.5	-0.1	Non-ruminant adipose fats
ROS-C-2188	320	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2189	320	IVb	Refitted, fine, decorated	63	C_{16}-C_{26}*	C_{18}-C_{24}	-	-	-	-	-	*nd*
ROS-C-2190	320	IVb	Single, fine, decorated	45	C_{16}-C_{28}*, C_{30}	-	C_{25}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
ROS-C-2191	320	IVb	Single, fine, decorated	10	-	-	-	-	-	-	-	*nd*
ROS-C-2192	320	IVb	Refitted, fine, decorated	19	-	-	-	-	-	-	-	*nd*
ROS-C-2193	320	IVb	Single, fine, decorated	292	C_{14}-C_{22}*, C_{24}-C_{30}	C_{14}, C_{18}-C_{24}*	-	-	-	-	-	*nd*
ROS-C-2194	65	IVb	Single, coarse, undecorated	64	C_{14}-C_{20}	-	-	-	-27.9	-24.8	3.1	Non-ruminant adipose fats
ROS-C-2195	65	IVb	Single, coarse, undecorated	20	C_{14}-C_{24}*, C_{29}-C_{30}	C_{16}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-2196	65	IVb	Refitted, fine, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2197	65	IVb	Single, fine, undecorated	109	C_{16}-C_{26}	C_{16}-C_{30}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and plant/beeswax
ROS-C-2198	68	IVb	Refitted, fine, decorated	32	C_{16}-C_{18}, C_{24}-C_{25}	C_{16}-C_{26}	-	-	-	-	-	Probably modern contamination
ROS-C-2199	68	IVb	Refitted, fine, decorated	76	C_{16}-C_{26}	C_{18}-C_{30}	C_{23}-C_{31}	B	-	-	-	Beeswax

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ROS-C-2200	60	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-2201	60	IVb	Single, coarse, undecorated	3338	C_{16}-C_{24}	-	-	-	-25.2	-26.1	-0.9	Mixture ruminant and non-ruminant adipose fats
ROS-C-2202	115	V	Single, fine, decorated	51	C_{16}-C_{28}	-	-	-	-	-	-	Animal fats
ROS-C-2203	322	V	Single, fine, decorated	98	C_{16}-C_{29}*	C_{18}-C_{30}	C_{25}-C_{31}	B	-	-	-	Mixture animal fats and beeswax
ROS-C-4667	3039	IVb	Refitted, coarse, undecorated	7	C_{14}-C_{26}	C_{14}-C_{26}	-	-	-	-	-	*nd*
ROS-C-4668	3039	IVb	Refitted, fine, decorated	171	C_{14}-C_{18}*, C_{20}-C_{26}	C_{12}-C_{28}	-	-	-25.6	-25.2	0.5	Non-ruminant adipose fats
ROS-C-4669	3039	IVb	Single, fine, decorated	33	C_{14}-C_{18}*, C_{24}	C_{12}-C_{30}	-	-	-	-	-	*nd*
ROS-C-4670	3039	IVb	Single, coarse, undecorated	99	C_{14}-C_{18}*, C_{20}-C_{22}	C_{14}-C_{20}, C_{22}	-	-	-27.1	-28.3	-1.2	Mixture ruminant and non-ruminant adipose fats
ROS-C-4671	3039	IVb	Single, coarse, undecorated	766	C_{14}-C_{20}	-	-	-	-26.3	-27.1	-0.8	Mixture ruminant and non-ruminant adipose fats
ROS-C-4672	3039	IVb	Single, coarse, undecorated	11	-	-	-	-	-	-	-	*nd*
ROS-C-4673	3039	IVb	Single, fine, decorated	36	C_{14}-C_{18}*, C_{22}-C_{26}	C_{12}-C_{28}	C_{27}-C_{31}	-	-	-	-	*nd*
ROS-C-4674	3039	IVb	Single, coarse, undecorated	161	C_{14}-C_{24}*	C_{13}-C_{20}*	-	-	-26.9	-27.7	-0.8	Mixture ruminant and non-ruminant adipose fats
ROS-C-4675	3039	IVb	Refitted, fine, decorated	12	C_{14}-C_{24}	C_{14}-C_{26}	-	-	-	-	-	Probably modern contamination
ROS-C-4676	3039	IVb	Refitted, coarse, undecorated	30	C_{14}-C_{26}*	C_{12}-C_{18}*, C_{20}-C_{26}	C_{29}-C_{31}	-	-	-	-	*nd*
ROS-C-4677	3039	IVb	Refitted, coarse, undecorated	260	C_{14}-C_{24}*	C_{12}-C_{18}*	-	-	-26.0	-27.0	-1.0	Mixture ruminant and non-ruminant adipose fats
ROS-C-4678	3009	IVb	Single, coarse, undecorated	4627	C_{13}-C_{19}*	-	-	-	-25.5	-26.2	-0.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-4679	3034	IVb	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ROS-C-4680	3034	IVb	Single, coarse, undecorated	400	C_{14}-C_{26}	-	-	-	-24.1	-25.8	-1.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-4681	3034	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-4682	3034	IVb	Single, coarse, undecorated	550	C_{14}-C_{24}	C_{18}-C_{26}	-	-	-27.1	-26.5	0.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-4683	3034	IVb	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-4684	3034	IVb	Single, fine, undecorated	5	-	-	-	-	-	-	-	-
ROS-C-4685	3034	IVb	Single, fine, decorated	149	C_{14}-C_{28}	C_{14}-C_{24}*, C_{26}-C_{30}	C_{23}-C_{31}	-	-27.2	-28.2	-1.0	Mixture ruminant and non-ruminant adipose fats
ROS-C-4686	3034	IVb	Single, fine, decorated	62	C_{14}-C_{26}	C_{16}-C_{30}	C_{25}-C_{31}	-	-27.2	-29.1	-1.9	Mixture ruminant and non-ruminant adipose fats
ROS-C-4687	3034	IVb	Single, fine, decorated	8	C_{14}-C_{26}*	C_{14}-C_{24}*, C_{26}-C_{28}	C_{25}-C_{31}	-	-	-	-	*nd*
ROS-C-4688	3034	IVb	Refitted, fine, decorated	14	C_{13}-C_{28}*, C_{30}	C_{14}-C_{28}	C_{27}-C_{31}	-	-28.2	-30.7	-2.4	Mixture ruminant and non-ruminant fats
ROS-C-4689	3034	IVb	Single, fine, decorated	110	C_{14}-C_{28}*	C_{15}-C_{26}*, C_{28}-C_{32}	C_{23}-C_{31}	B	-	-	-	Mixture animal fats and beeswax
ROS-C-4690	3034	IVb	Refitted, fine, decorated	1672	C_{14}-C_{20}	-	-	-	-26.0	-26.0	0.0	Non-ruminant fats
ROS-C-4691	3034	IVb	Single, fine, decorated	54	C_{14}-C_{22}*	C_{14}-C_{28}, C_{30}-C_{32}	C_{23}-C_{25}	B	-	-	-	Mixture animal fats and beeswax
ROS-C-4692	3034	IVb	Single, fine, decorated	112	C_{14}-C_{26}*, C_{28}	C_{12}-C_{24}*, C_{26}-C_{30}	C_{23}-C_{29}	-	-27.0	-27.9	-0.9	Mixture ruminant and non-ruminant adipose fats
ROS-C-4693	3034	IVb	Single, fine, decorated	75	C_{14}-C_{26}*	C_{12}-C_{26}*	C_{23}-C_{31}	-	-	-	-	*nd*
ROS-C-4694	3011	IVb	Single, coarse, undecorated	1452	C_{13}-C_{20}*, C_{22}-C_{26}	C_{14}	-	-	-24.7	-24.9	-0.2	Non-ruminant fats
ROS-C-4695	3011	IVb	Single, coarse, undecorated	17246	C_{14}-C_{19}*	-	-	-	-27.0	-28.6	-1.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-4696	3011	IVb	Single, coarse, undecorated	15	C_{14}-C_{30}*	C_{14}-C_{22}*, C_{24}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-4697	3011	IVb	Single, fine, decorated	6	-	-	-	-	-	-	-	-
ROS-C-4698	3011	IVb	Single, coarse, undecorated	191	C_{14}-C_{24}*	C_{12}-C_{18}*	-	-	-28.2	-29.8	-1.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-4699	3011	IVb	Refitted, coarse, undecorated	25	C_{15}-C_{24}*	C_{15}-C_{24}*	C_{19}-C_{23}*	-	-	-	-	Probably modern contamination
ROS-C-4700	3011	IVb	Single, coarse, undecorated	836	C_{14}-C_{20}*, C_{22}	-	-	-	-25.0	-25.0	0.0	Non-ruminant fats
ROS-C-4701	3011	IVb	Single, coarse, undecorated	1231	C_{13}-C_{24}*	-	-	-	-26.9	-27.7	-0.8	Mixture ruminant and non-ruminant adipose fats
ROS-C-4702	3011	IVb	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
ROS-C-4703	3011	IVb	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ROS-C-4704	3011	IVb	Refitted, fine, decorated	11	C_{15}-C_{24}*	C_{14}-C_{22}*	-	-	-	-	-	Probably modern contamination
ROS-C-4705	3011	IVb	Single, fine, decorated	23	C_{24}-C_{26}	C_{12}-C_{22}*, C_{24}	-	-	-	-	-	Probably modern contamination
ROS-C-4706	3011	IVb	Single, coarse, undecorated	37	C_{14}-C_{26}*, C_{28}	C_{16}-C_{24}*, C_{26}-C_{30}	C_{25}-C_{31}	-	-27.1	-27.9	-0.9	Mixture ruminant and non-ruminant adipose fats

Appendix 6-7: Proportion of domesticated animals in number of remains (NR) and weight of remains (WR) for all LBK, Grossgartach and Roessen sites studied in the Alsace region. Adapted from, Arbogast (1992, 2000, unpublished data from Bischoffsheim); Lefranc and Michler (2015) and Jeunesse and Arbogast (1997).

LBK Bischoffsheim		Early LBK		Middle LBK		Late LBK	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		13.3	26.3	7.1	8.7	7.6	24.5
Total domesticate		86.7	73.7	92.9	91.3	92.4	75.5
% animals inside domesticate	Cattle	46.5	76.8	35.9	69.7	25.9	10.1
	Pig	30.7	14.1	43.6	23.3	40.3	79.3
	Sheep/goat	22.8	9.1	20.5	7.0	33.7	10.6
	Other	0	0	0	0	0	0

LBK Rosheim		"Sainte Odile"		"Rittergass"		Localities combined	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		6.8	25.7	3.0	28.0	4.9	26.9
Total domesticate		93.2	74.3	97.0	72.0	95.1	73.1
% animals inside domesticate	Cattle	34.5	61.9	38.8	67.0	36.7	64.4
	Pig	40.3	25.9	32.0	18.5	36.1	22.3
	Sheep/goat	24.9	12.1	27.3	14.0	26.1	13.0
	Others	0.3	0.1	1.9	0.5	1.1	0.0

Grossgartach Rosheim		"Sandgrube & Mittelweg"		"Laser"		Localities combined	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		8.4	13.9	5.1	8.9	7.7	13.3
Total domesticate		91.6	86.7	94.9	91.1	92.3	86.7
% animals inside domesticate	Cattle	62.3	83.0	55.0	79.3	61.4	82.5
	Pig	25.7	13.1	34.5	16.0	26.8	13.5
	Sheep/goat	11.9	3.8	10.5	4.3	11.7	3.9
	Other	0.1	0.1	0	0	0.1	0

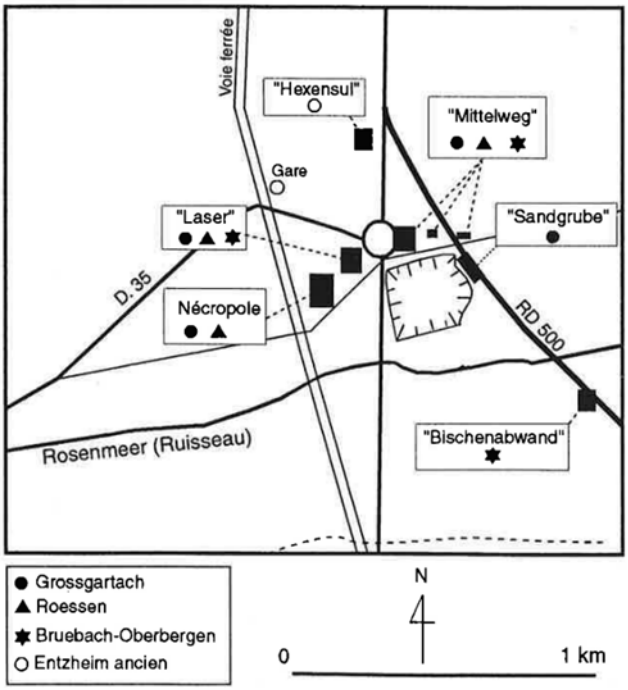
Roessen Rosheim		"Mittelweg"		"Laser"		Localities combined	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		4.7	5.6	8.9	12.9	5.2	6.9
Total domesticate		95.3	94.4	91.1	87.1	94.8	93.1
% animals inside domesticate	Cattle	59.2	73.9	72.5	90.9	60.6	77.4
	Pig	33.3	18.5	15.7	1.8	31.3	15.8
	Sheep/goat	7.5	7.4	11.8	2.9	7.9	6.7
	Other	0.2	0	0	0	0.2	0

LBK Colmar		Early LBK		Middle LBK		Late LBK	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		8.5	32.5	3.2	22.3	25.0	25.0
Total domesticate		90.5	67.5	86.8	77.7	75.0	75.0
% animals inside domesticate	Cattle	48.1	69.6	42.9	25.0	33.3	10.1
	Pig	29.6	15.2	28.6	37.5	33.3	79.3
	Sheep/goat	22.2	15.2	28.6	12.5	33.3	10.6
	Other	0.0	0.0	0.0	0.0	0.0	0

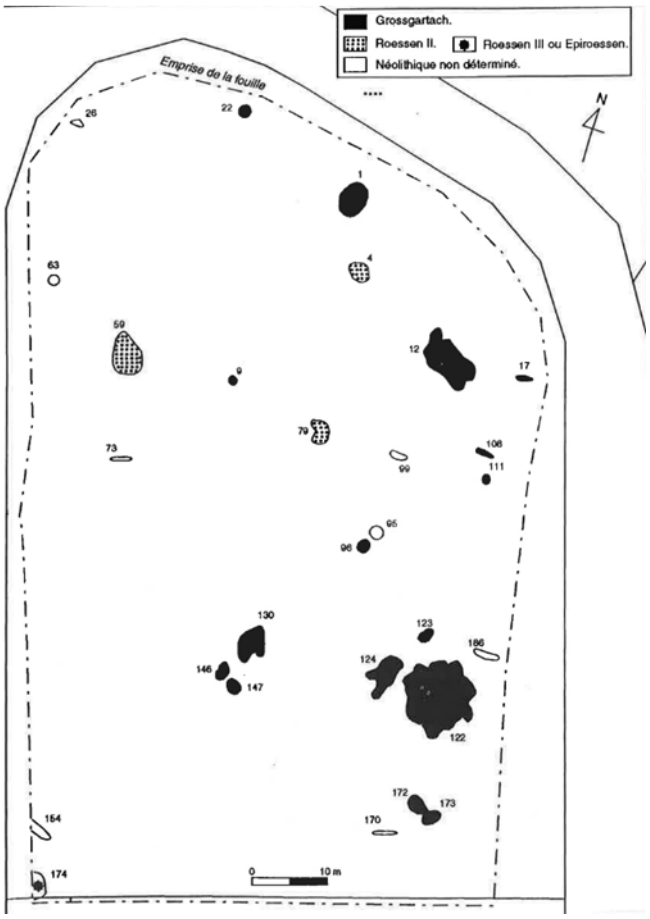
LBK Ensisheim		Early LBK		Middle LBK		Late LBK	
		NISP (%)	WR (%)	NISP (%)	WR (%)	NISP (%)	WR (%)
Total wild		5.9	0.7	4.5	2.7	11.9	5.6
Total domesticate		94.2	99.3	96.1	97.3	88.3	96.5
% animals inside domesticate	Cattle	82.8	53.6	83.8	33.1	73.4	10.1
	Pig	9.6	11.1	6.1	24.3	16.1	79.3
	Sheep/goat	7.7	34.7	10.2	42.4	10.5	10.6
	Other	0	0.6	0	0.2	0.1	0

Appendix 6-8: (a) Overall site plan of Rosheim settlement showing occupation of Grossgartach and Roessen groups. (b) Site plan of Rosheim "Laser" showing occupation of Grossgartach and Roessen groups. From Lefranc *et al.* (1999, Figures 2 and 4).

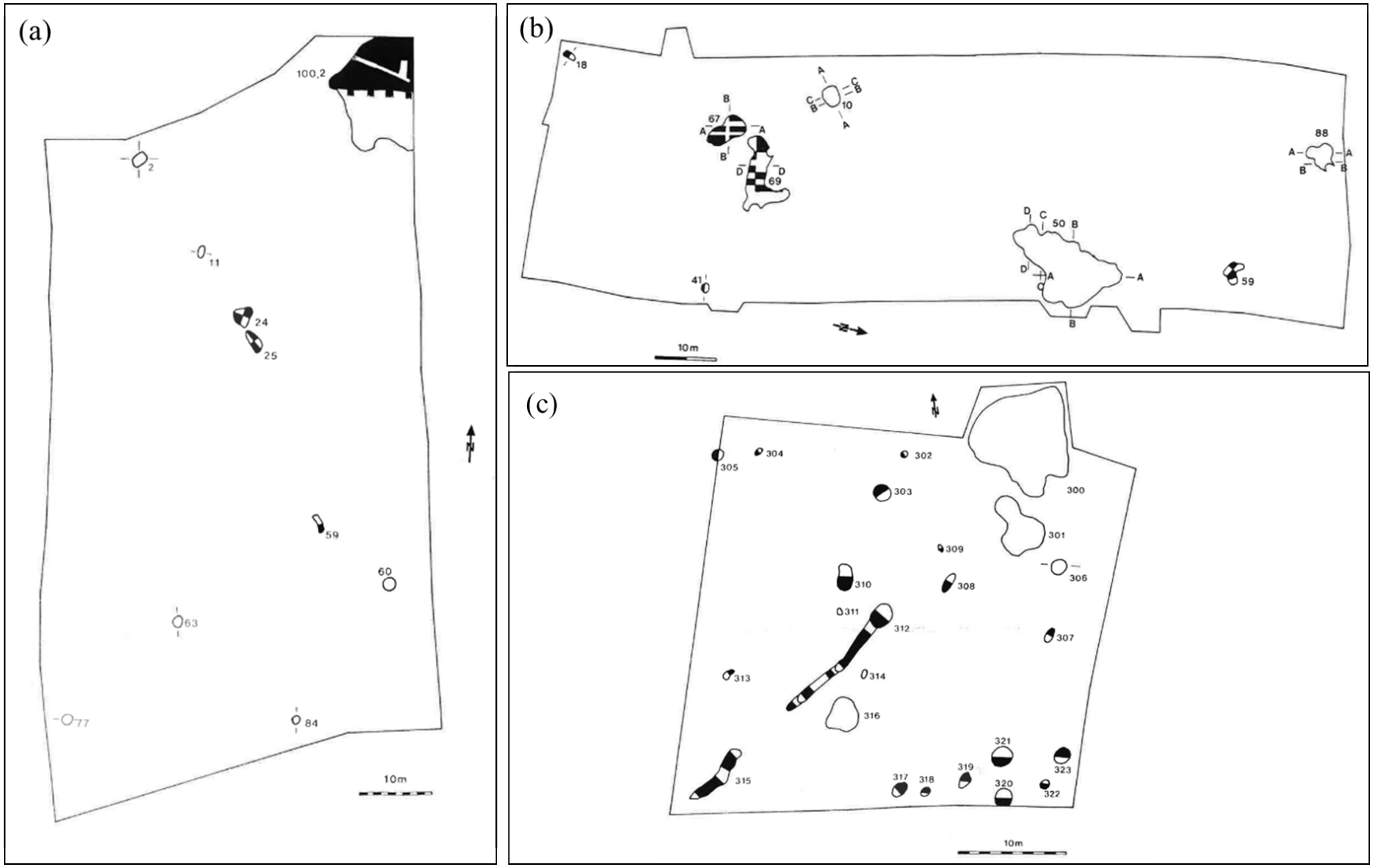
(a)



(b)



Appendix 6-9: Site plan of Rosheim “Mittelweg and Sandgrube” with occupation of Grossgartach (a) and (b) and Roessen (c). Black parts are unexcavated and white are excavated. From Jeunesse and Arbogast (1996, Appendices 1, 2 and 3).



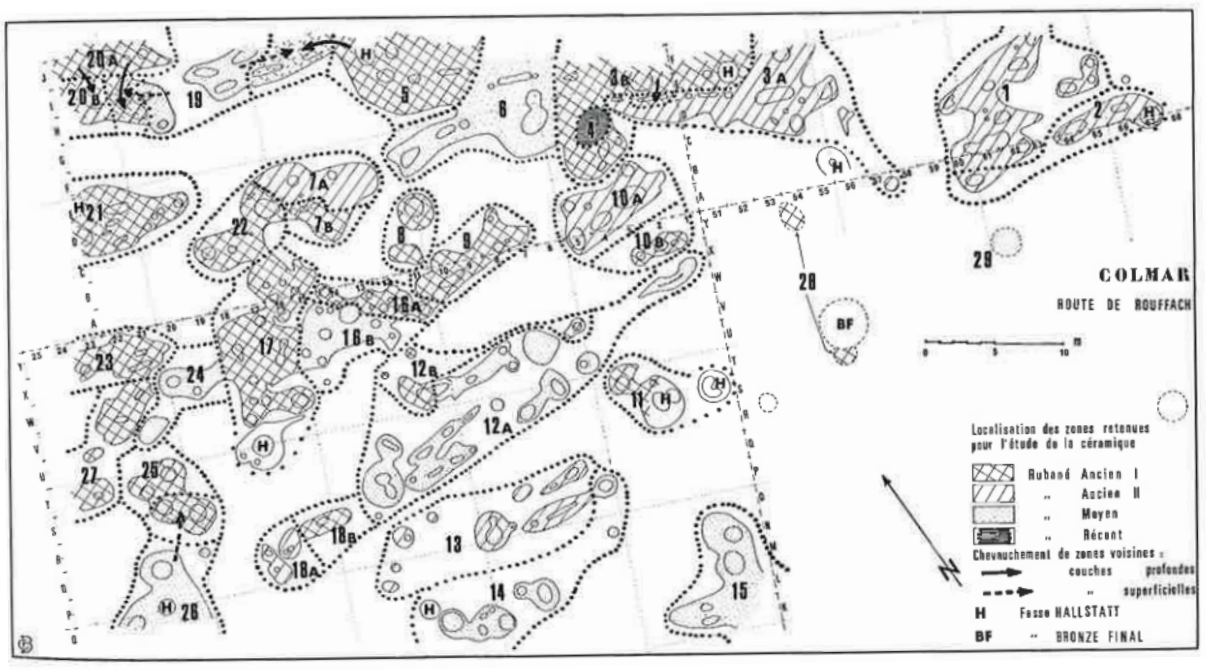
Appendix 6-10: Potsherds characteristics and results of ORA at the site of Rosheim "Laser, Mittelweg, Sandgrube". The codes are analogous to those given in Appendix 6.5.

Sherd #	Pit	Groupe	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ROS-C-4581	59	Roe.	Single, fine, undecorated	8	C_{12}-C_{18}	C_{12}-C_{18}	-	-	-	-	-	Probably modern contamination
ROS-C-4582	59	Roe.	Refitted, fine, undecorated	70	C_{12}-C_{28}	C_{12}-C_{30}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-4583	59	Roe.	Single, fine, decorated	25	-	-	-	-	-	-	-	*nd*
ROS-C-4584	59	Roe.	Refitted, fine, decorated	15	-	-	-	-	-	-	-	*nd*
ROS-C-4585	59	Roe.	Single, fine, decorated	92	C_{14}-C_{24}	C_{14}-C_{20}	-	-	-	-	-	Probably modern contamination
ROS-C-4586	59	Roe.	Refitted, fine, decorated	1191	C_{14}-C_{22}*	-	-	T	-27.8	-33.1	-5.3	Dairy fats and resin?
ROS-C-4587	59	Roe.	Single, fine, decorated	176	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4588	4	Roe.	Single, fine, undecorated	66	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4589	172	Gros.	Single, coarse, undecorated	387	C_{14}-C_{20}*, C_{22}-C_{28}	C_{24}-C_{32}	-	-	-26.5	-28.8	-2.3	Ruminant adipose fats
ROS-C-4590	172	Gros.	Refitted, coarse, undecorated	20	C_{14}-C_{26}*, C_{28}	-	-	-	-	-	-	*nd*
ROS-C-4591	122	Gros.	Refitted, coarse, undecorated	17	C_{14}-C_{26}*, C_{28}	C_{12}-C_{22}, C_{26}	-	-	-	-	-	Animal fats?
ROS-C-4592	122	Gros.	Single, coarse, undecorated	9	C_{14}-C_{18}	-	-	-	-	-	-	Animal fats?
ROS-C-4593	122	Gros.	Single, coarse, undecorated	19	C_{14}-C_{30}	C_{16}-C_{18}, C_{26}	-	-	-	-	-	Animal fats
ROS-C-4594	122	Gros.	Single, coarse, undecorated	18	C_{16}-C_{18}	-	-	-	-	-	-	Animal fats
ROS-C-4595	122	Gros.	Single, coarse, undecorated	14	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4596	122	Gros.	Single, coarse, undecorated	973	C_{14}-C_{18}*, C_{20}	-	-	-	-26.9	-29.6	-2.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-4597	122	Gros.	Single, coarse, undecorated	10	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4598	63	Gros.	Single, coarse, undecorated	7	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4599	63	Gros.	Single, coarse, undecorated	12	-	-	-	-	-	-	-	*nd*
ROS-C-4600	63	Gros.	Refitted, coarse, undecorated	4163	C_{14}-C_{20}*, C_{24}	C_{24}-C_{30}	-	-	-27.1	-29.4	-2.3	Mixture ruminant and non-ruminant adipose fats
ROS-C-4601	63	Gros.	Single, coarse, undecorated	137	C_{14}-C_{30}	C_{24}-C_{34}	C_{27}-C_{31}	B	-	-	-	Beeswax
ROS-C-4602	63	Gros.	Single, coarse, undecorated	812	C_{14}-C_{24}*	-	-	-	-25.4	-25.2	0.1	Non-ruminant adipose fats
ROS-C-4603	63	Gros.	Refitted, fine, undecorated	1103	C_{14}-C_{24}*, C_{26}	C_{14}-C_{20}	-	-	-26.2	-28.5	-2.3	Mixture ruminant and non-ruminant adipose fats
ROS-C-4604	63	Gros.	Refitted, fine, decorated	105	C_{14}-C_{26}*, C_{28}-C_{30}	C_{14}-C_{20}	C_{21}-C_{29}	-	-27.8	-29.9	-2.1	Mixture ruminant and non-ruminant adipose fats
ROS-C-4605	77	Gros.	Single, fine, decorated	327	C_{14}-C_{24}*	C_{14}-C_{24}*, C_{26}		-	-	-	-	Animal fats?
ROS-C-4606	77	Gros.	Refitted, fine, decorated	387	C_{14}-C_{26}*, C_{28}	C_{12}-C_{22}*, C_{24}-C_{32}	C_{23}-C_{31}	B	-	-	-	Mixture animal fats and beeswax
ROS-C-4607	77	Gros.	Single, coarse, undecorated	1314	C_{14}-C_{30}	C_{24}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-4608	77	Gros.	Single, coarse, undecorated	11	C_{16}-C_{26}*	-	-	-	-	-	-	Probably modern contamination
ROS-C-4609	77	Gros.	Single, coarse, undecorated	381	C_{14}-C_{28}*	C_{24}-C_{32}	C_{25}-C_{29}	-	-	-	-	Beeswax?
ROS-C-4610	77	Gros.	Single, coarse, undecorated	388	C_{14}-C_{28}*, C_{30}	C_{14}-C_{32}	C_{23}-C_{31}	-	-26.9	-30.3	-3.4	Mixture dairy and non-ruminant adipose fats
ROS-C-4611	77	Gros.	Single, coarse, undecorated	117	C_{14}-C_{28}*, C_{30}-C_{32}	C_{12}-C_{28}*, C_{30}-C_{32}	-	-	-	-	-	*nd*
ROS-C-4612	300	Roe.	Refitted, fine, decorated	603	C_{12}-C_{24}*	C_{12}-C_{22}*, C_{24}-C_{26}	-	-	-	-	-	Animal fats
ROS-C-4613	300	Roe.	Refitted, coarse, undecorated	697	C_{14}-C_{26}*, C_{28}	C_{18}, C_{24}-C_{32}	C_{23}-C_{31}	-	-27.5	-32.5	-5.0	Dairy fats
ROS-C-4614	300	Roe.	Refitted, coarse, undecorated	391	C_{12}-C_{26}*, C_{28}-C_{30}	C_{12}-C_{32}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and plants/beeswax?
ROS-C-4615	300	Roe.	Single, coarse, undecorated	428	C_{14}-C_{28}*, C_{30}-C_{32}	C_{22}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-4616	300	Roe.	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ROS-C-4617	300	Roe.	Single, coarse, undecorated	572	C_{14}-C_{26}*, C_{28}-C_{30}	C_{14}-C_{32}	C_{23}-C_{31}	B	-27.1	-32.2	-5.1	Dairy fats and beeswax
ROS-C-4618	300	Roe.	Refitted, coarse, undecorated	201	C_{14}-C_{28}	C_{16}-C_{32}	C_{23}-C_{29}	-	-28.3	-32.6	-4.3	Dairy fats
ROS-C-4619	300	Roe.	Single, coarse, undecorated	677	C_{14}-C_{26}*, C_{28}	C_{18}-C_{32}	C_{25}-C_{29}	-	-29.4	-33.1	-3.7	Dairy fats
ROS-C-4620	300	Roe.	Single, fine, undecorated	18	C_{14}-C_{18}	C_{12}-C_{24}	-	-	-	-	-	*nd*
ROS-C-4621	300	Roe.	Single, fine, undecorated	40	C_{14}-C_{24}	C_{16}-C_{28}	-	-	-	-	-	*nd*
ROS-C-4622	200	Roe.	Single, coarse, undecorated	1183	C_{14}-C_{26}*	C_{24}-C_{28}, C_{25}	-	-	-27.8	-32.6	-4.8	Dairy fats
ROS-C-4623	200	Roe.	Single, coarse, undecorated	137	C_{14}-C_{25}*, C_{26}	C_{14}-C_{30}	C_{27}-C_{31}	-	-	-	-	Probably modern contamination
ROS-C-4624	200	Roe.	Single, coarse, undecorated	632	C_{14}-C_{19}*	C_{14}-C_{32}	-	-	-	-	-	Animal fats

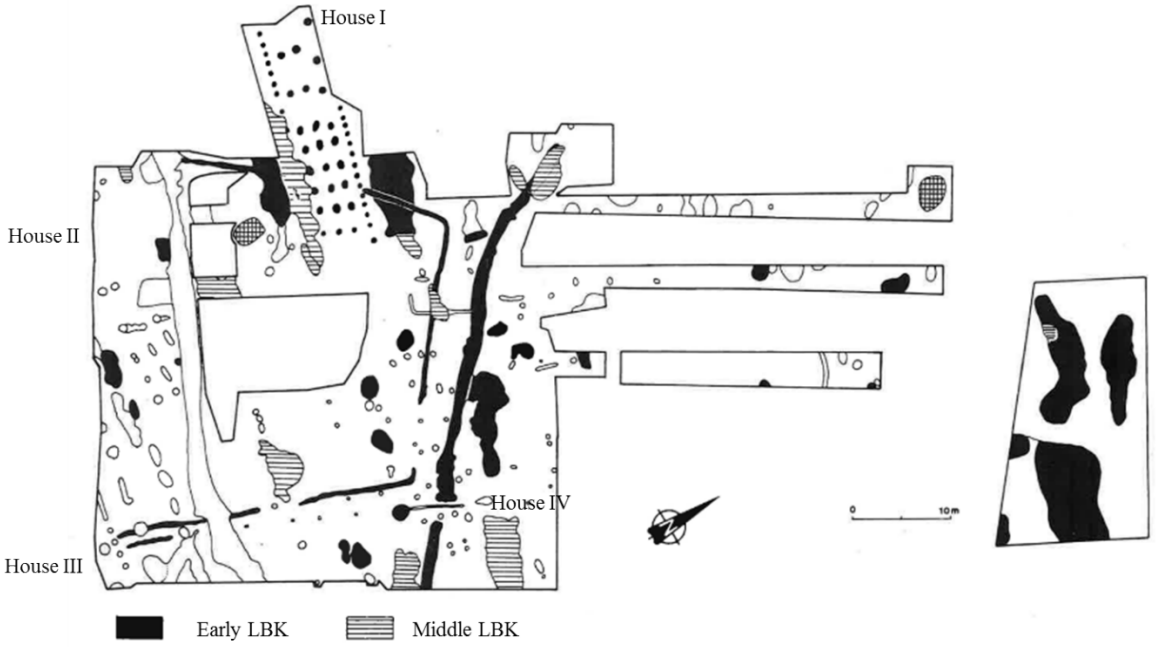
Sherd #	Pit	Groupe	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ROS-C-4625	200	Roe.	Single, coarse, undecorated	876	C_{14}-C_{26}*, C_{28}	C_{16}-C_{32}	C_{23}-C_{31}	B	-	-	-	Mixture animal fats and beeswax
ROS-C-4626	200	Roe.	Single, coarse, undecorated	864	C_{16}-C_{20}*	-	-		-30.1	-32.2	-2.2	Ruminant adipose fats
ROS-C-4627	200	Roe.	Refitted, coarse, undecorated	264	C_{14}-C_{23}*	C_{14}-C_{18}	-	-	-29.9	-31.9	-2.0	Ruminant adipose fats
ROS-C-4628	200	Roe.	Single, coarse, undecorated	714	C_{14}-C_{20}*	-	-	-	-26.6	-27.3	-0.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-4629	200	Roe.	Single, coarse, undecorated	2032	C_{14}-C_{22}*	-	-	-	-28.9	-32.2	-3.2	Dairy fats
ROS-C-4630	200	Roe.	Single, fine, decorated	57	C_{14}-C_{18}	C_{14}-C_{20}	-	-	-	-	-	*nd*
ROS-C-4631	200	Roe.	Single, coarse, undecorated	57	-	-	-	-	-	-	-	Probably modern contamination
ROS-C-4632	200	Roe.	Single, coarse, undecorated	6	C_{14}-C_{26}*, C_{28}	C_{14}-C_{30}	C_{27}-C_{29}	-	-	-	-	Mixture animal fats and plants/beeswax?
ROS-C-4633	50	Gros.	Single, fine, decorated	226	C_{14}-C_{18}*, C_{20}	-	-	-	-	-	-	*nd*
ROS-C-4634	50	Gros.	Single, fine, decorated	223	C_{12}-C_{18}*, C_{20}	C_{12}-C_{24}	-	-	-	-	-	*nd*
ROS-C-4635	50	Gros.	Refitted, fine, decorated	502	C_{14}-C_{24}*, C_{26}-C_{28}	C_{12}-C_{18}*, C_{20}-C_{32}	C_{23}-C_{31}	-	-	-	-	Beeswax?
ROS-C-4636	50	Gros.	Refitted, fine, decorated	10	C_{14}-C_{18}	C_{14}-C_{24}	-	-	-	-	-	*nd*
ROS-C-4637	50	Gros.	Refitted, fine, decorated	121	C_{13}-C_{16}*	C_{12}-C_{22}*, C_{24}-C_{26}	C_{25}-C_{29}	-	-	-	-	*nd*
ROS-C-4638	50	Gros.	Refitted, fine, decorated	3048	C_{14}-C_{24}*, C_{26}	C_{14}-C_{20}*, C_{22}-C_{30}	C_{23}-C_{29}	-	-25.8	-25.6	0.2	Non-ruminant adipose fats
ROS-C-4639	50	Gros.	Single, fine, decorated	56	C_{14}-C_{20}	C_{14}-C_{22}*, C_{24}	-	-	-	-	-	*nd*
ROS-C-4640	50	Gros.	Refitted, fine, decorated	89	C_{12}-C_{26}*	C_{12}-C_{24}*	-	-	-	-	-	*nd*
ROS-C-4641	50	Gros.	Refitted, fine, decorated	189	C_{14}-C_{26}*	C_{14}-C_{26}	C_{21}-C_{29}	-	-25.8	-22.7	3.1	Non-ruminant adipose fats
ROS-C-4642	50	Gros.	Single, fine, decorated	0	C_{14}-C_{24}	C_{13}-C_{24}*	-	-	-25.8	-27.5	-1.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-4643	50	Gros.	Refitted, fine, decorated	68	C_{14}-C_{20}*	-	-	-	-25.0	-24.7	0.3	Non-ruminant fats
ROS-C-4644	50	Gros.	Single, fine, decorated	6064	C_{14}-C_{24}*	-	-	-	-26.5	-28.9	-2.4	Mixture ruminant and non-ruminant adipose fats
ROS-C-4645	50	Gros.	Refitted, fine, undecorated	1811	C_{14}-C_{20}*	-	-	-	-28.0	-30.2	-2.3	Mixture ruminant and non-ruminant adipose fats
ROS-C-4646	50	Gros.	Single, fine, undecorated	2116	C_{14}-C_{20}*	-	-	-	-27.6	-30.0	-2.4	Mixture ruminant and non-ruminant adipose fats
ROS-C-4647	50	Gros.	Single, fine, undecorated	92	C_{14}-C_{26}*	C_{14}-C_{20}	C_{23}-C_{31}	-	-	-	-	Plants?
ROS-C-4648	50	Gros.	Refitted, fine, undecorated	1001	C_{14}-C_{26}*	C_{14}-C_{18}	-	-	-27.0	-24.6	2.4	Non-ruminant fats
ROS-C-4649	50	Gros.	Single, fine, undecorated	2596	C_{14}-C_{24}*	-	-	-	-26.1	-28.6	-2.5	Mixture ruminant and non-ruminant adipose fats
ROS-C-4650	50	Gros.	Single, fine, undecorated	439	C_{14}-C_{26}*	C_{14}-C_{26}	C_{23},C_{29}	-	-26.3	-31.3	-5.0	Mixture dairy and non-ruminant adipose fats
ROS-C-4651	50	Gros.	Single, fine, undecorated	1377	C_{14}-C_{22}*	-	-	-	-24.9	-26.5	-1.6	Mixture ruminant and non-ruminant adipose fats
ROS-C-4652	50	Gros.	Single, coarse, undecorated	15	C_{16}-C_{26}	C_{14}-C_{18}	-	-	-	-	-	*nd*
ROS-C-4653	50	Gros.	Single, coarse, undecorated	122	C_{14}-C_{26}*	C_{14}-C_{20}	-	-	-	-	-	Animal fats
ROS-C-4654	50	Gros.	Single, coarse, undecorated	33	C_{14}-C_{22}*, C_{24}-C_{26}	C_{14}-C_{18}	-	-	-29.6	-27.6	2.0	Non-ruminant fats?
ROS-C-4655	50	Gros.	Single, coarse, undecorated	190	C_{14}-C_{24}*, C_{26}-C_{28}	-	-	-	-25.8	-26.7	-0.8	Mixture ruminant and non-ruminant adipose fats
ROS-C-4656	50	Gros.	Single, coarse, undecorated	838	C_{14}-C_{26}*	-	-	-	-26.6	-28.8	-2.3	Mixture ruminant and non-ruminant adipose fats
ROS-C-4657	50	Gros.	Single, coarse, undecorated	1914	C_{14}-C_{26}*	-	-	-	-26.8	-28.7	-1.8	Mixture ruminant and non-ruminant adipose fats
ROS-C-4658	50	Gros.	Single, coarse, undecorated	190	C_{14}-C_{24}*, C_{26}-C_{30}	-	-	-	-26.7	-28.7	-2.1	Mixture ruminant and non-ruminant adipose fats
ROS-C-4659	50	Gros.	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
ROS-C-4660	50	Gros.	Single, coarse, undecorated	17	C_{14}*-C_{18}	C_{13}-C_{16}	-	-	-	-	-	Probably modern contamination
ROS-C-4661	50	Gros.	Single, coarse, undecorated	221	C_{14}-C_{20}*, C_{22}-C_{24}	C_{12}-C_{30}	C_{23}-C_{31}	-	-28.8	-29.6	-0.7	Mixture ruminant and non-ruminant adipose fats
ROS-C-4662	50	Gros.	Single, coarse, undecorated	22	C_{14}-C_{26}*, C_{28}	C_{12}-C_{20}	-	-	-	-	-	Animal fats
ROS-C-4663	50	Gros.	Single, coarse, undecorated	788	C_{14}-C_{24}*, C_{26}-C_{30}	C_{24}-C_{32}	C_{23}-C_{31}	B	-	-	-	Beeswax
ROS-C-4664	50	Gros.	Single, coarse, undecorated	917	C_{14}-C_{26}*	C_{14}-C_{18}	-	-	-24.7	-23.5	1.2	Non-ruminant adipose fats
ROS-C-4665	50	Gros.	Single, coarse, undecorated	602	C_{14}-C_{26}	-	-	-	-25.5	-25.7	-0.2	Non-ruminant adipose fats
ROS-C-4666	50	Gros.	Single, coarse, undecorated	159	C_{14}-C_{24}*, C_{26}-C_{30}	C_{16}, C_{24}-C_{32}	C_{21}-C_{29}	B	-	-	-	Beeswax

Appendix 6-11: Site Plan of Colmar "Route de Rouffach". (a) Excavation 1977-1984 showing the zones of pottery assemblages (from Bonnet *et al.* 1988, Figure3). (b) Excavation 1985-1986 showing early and middle LBK assemblages (adapted from Jeunesse 1993b, Figure 7).

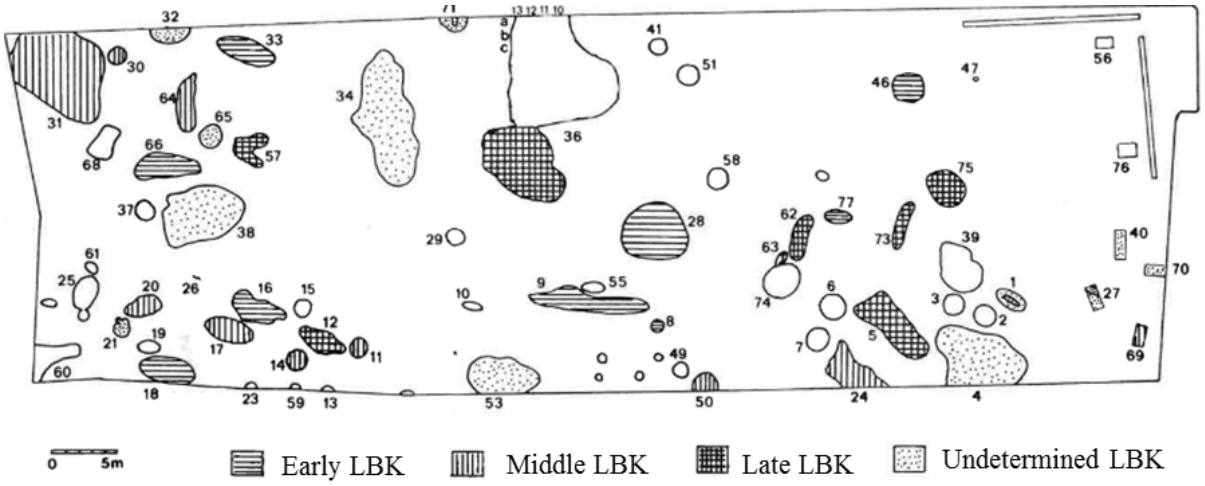
(a)



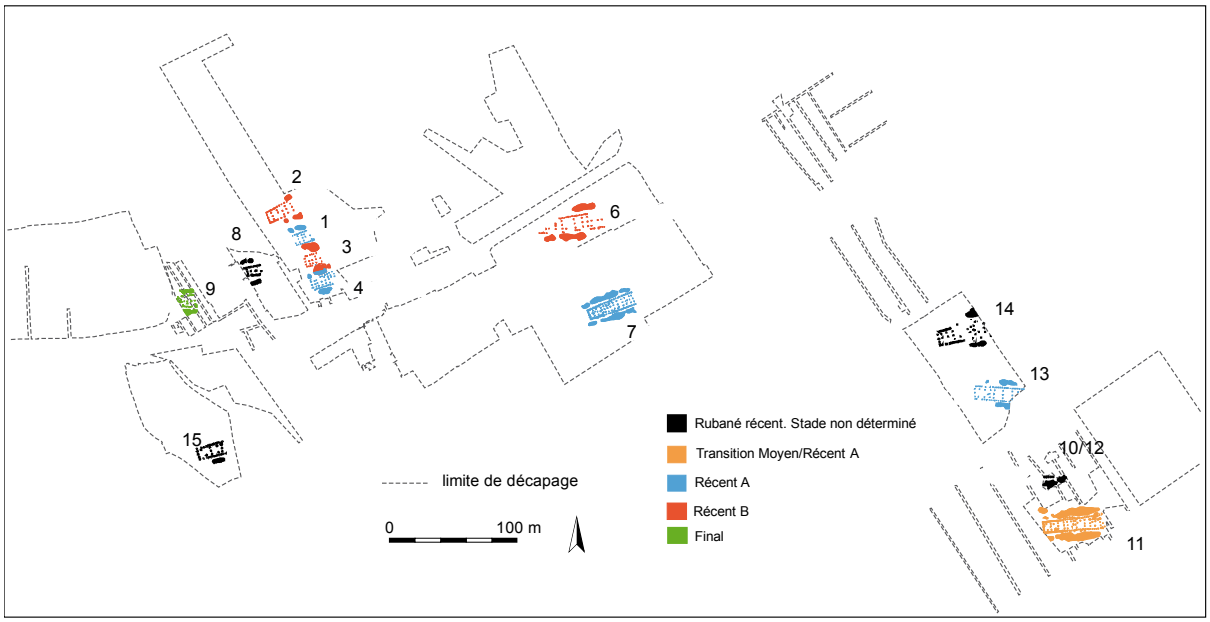
(b)



Appendix 6-12: Site Plan of Ensisheim “Ratfeld”. Adapted from Jeunesse and Sainty (1992, Figure 5).



Appendix 6-13: Site Plan of Sierentz “Sandgrube and Tiergarten” showing recent and final LBK settlements. Courtesy of P. Lefranc.



Appendix 6-14: Potsherds characteristics and results of ORA at the site of Colmar "Route de Rouffach". The codes are analogous to those given in Appendix 6.5.

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
COL-C-6021	4	IV	Single, coarse, undecorated	13	C_{16}-C_{18}	C_{14}-C_{20}	-	-	-	-	-	Probable modern contamination
COL-C-6022	4	IV	Refitted, coarse, undecorated	6	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6023	4	IV	Single, coarse, undecorated	13	C_{14}-C_{18}	-	-	-	-	-	-	Probable modern contamination
COL-C-6024	4	IV	Single, coarse, undecorated	5	C_{16}-C_{26}	C_{24}-C_{26}	C_{21}-C_{33}*	-	-	-	-	*nd*
COL-C-6025	4	IV	Single, coarse, undecorated	6	C_{16}-C_{26}	-	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6026	4	IV	Single, coarse, undecorated	12	C_{16}-C_{24}*, C_{26}	-	C_{21}-C_{29}	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6027	4	IV	Refitted, fine, decorated	20	C_{16}-C_{24}	C_{16}-C_{26}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and beeswax/plant?
COL-C-6028	4	IV	Refitted, fine, decorated	32	C_{14}-C_{18}	C_{16}-C_{18}	-	-	-	-	-	*nd*
COL-C-6029	4	IV	Single, fine, decorated	35	C_{14}-C_{26}	C_{14}-C_{16}	-	-	-	-	-	Mixture animal fats and beeswax/plant?
COL-C-6030	4	IV	Single, fine, decorated	10	-	-	-	-	-	-	-	*nd*
COL-C-6031	4	IV	Single, fine, decorated	8	C_{16}-C_{18}	-	-	-	-	-	-	*nd*
COL-C-6032	15	III	Single, coarse, undecorated	12	C_{16}-C_{18}, C_{20}-C_{26}*	C_{16}-C_{20}	C_{21}-C_{27}*	-	-	-	-	Probable modern contamination
COL-C-6033	15	III	Single, coarse, undecorated	7	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6034	15	III	Single, coarse, undecorated	21	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6035	15	III	Fine, undecorated	911	C_{16}-C_{26}*	-	-	-	-28.6	-28.7	-0.1	-
COL-C-6036	15	III	Single, fine, decorated	23	C_{16}-C_{24}*, C_{26}	-	C_{19}-C_{29}*	-	-	-	-	-
COL-C-6037	15	III	Fine, undecorated	11	C_{16}-C_{24}*, C_{26}	-	C_{19}-C_{31}*	-	-	-	-	-
COL-C-6038	15	III	Single, fine, decorated	489	C_{14}-C_{20}*, C_{22}-C_{24}	C_{14}-C_{20}	C_{22}-C_{27}*	-	-	-	-	-
COL-C-6039	15	III	Single, fine, decorated	38	C_{14}-C_{24}*, C_{26}	C_{16}-C_{18}	-	-	-	-	-	-
COL-C-6040	15	III	Single, fine, decorated	66	$C1_6$-C_{28}*	C_{16}-C_{18}	C_{19}-C_{25}*	-	-	-	-	-
COL-C-6041	19	III	Single, coarse, undecorated	21	-	-	-	-	-	-	-	-
COL-C-6042	19	III	Single, coarse, undecorated	492	C_{14}-C_{28}*	C_{14}-C_{16}	C_{18}-C_{23}*	-	-27.2	-29.8	-2.6	-
COL-C-6043	19	III	Single, coarse, undecorated	18	C_{14}-C_{22}*	C_{14}-C_{26}	C_{19}-C_{31}*	-	-	-	-	-
COL-C-6044	19	III	Single, coarse, undecorated	32	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6045	19	III	Single, fine, decorated	37	C_{14}-C_{26}*	C_{16}-C_{18}	C_{19}-C_{31}*	-	-	-	-	Probable modern contamination
COL-C-6046	19	III	Single, fine, decorated	17	C_{14}-C_{30}*	C_{14}-C_{30}	C_{16}-C_{29}*	K	-	-	-	Plants?
COL-C-6047	19	III	Refitted, fine, decorated	9	-	-	-	-	-	-	-	*nd*
COL-C-6048	19	III	Single, fine, decorated	1	-	-	-	-	-	-	-	-
COL-C-6049	19	III	Single, coarse, undecorated	23	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6050	6	III	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6051	6	III	Single, fine, decorated	9	-	-	-	-	-	-	-	*nd*
COL-C-6052	6	III	Single, fine, decorated	11	C_{16}-C_{28}*	C_{16}-C_{18}	-	-	-	-	-	-
COL-C-6053	6	III	Single, fine, decorated	23	C_{16}-C_{26}*	C_{14}-C_{28}	C_{23}-C_{31}	-	-	-	-	-
COL-C-6054	6	III	Single, fine, decorated	10	-	-	-	-	-	-	-	-
COL-C-6055	6	III	Single, coarse, undecorated	4	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6056	6	III	Single, coarse, undecorated	943	C_{14}-C_{26}*	C_{24}-C_{30}	-	-	-25.8	-28.2	-2.4	Mixture ruminant and non-ruminant adipose fats
COL-C-6057	6	III	Single, coarse, undecorated	8	C_{16}-C_{25}*	-	-	-	-	-	-	Probable modern contamination
COL-C-6058	6	III	Single, coarse, undecorated	3	-	-	-	-	-25.6	-25.6	0.0	???
COL-C-6059	6	III	Single, coarse, undecorated	26	C_{16}-C_{30}*, C_{32}	C_{16}-C_{30}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6060	6	III	Single, coarse, undecorated	61	C_{16}-C_{28}*	C_{16}	-	K	-25.9	-29.2	-3.3	Mixture dairy and non-ruminant adipose fats
COL-C-6061	12A	III	Single, fine, decorated	1	-	-	-	-	-	-	-	-
COL-C-6062	12A	III	Single, fine, decorated	2	-	-	-	-	-	-	-	-
COL-C-6063	12A	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6064	12A	III	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
COL-C-6065	12A	III	Single, coarse, undecorated	697	C_{14}-C_{26}	-	-	-	-24.0	-25.9	-1.9	Mixture ruminant and non-ruminant adipose fats
COL-C-6066	12A	III	Single, coarse, undecorated	301	C_{14}-C_{26}*	-	-	K	-27.7	-29.4	-1.7	Mixture ruminant and non-ruminant adipose fats
COL-C-6067	12A	III	Single, coarse, undecorated	5	C_{16}-C_{28}*, C_{30}	C_{14}-C_{28}	-	-	-	-	-	*nd*
COL-C-6068	12A	III	Single, fine, undecorated	5	-	-	-	-	-	-	-	*nd*
COL-C-6069	12A	III	Refitted, fine, decorated	9	-	-	-	-	-	-	-	*nd*
COL-C-6070	12A	III	Single, fine, decorated	5	-	-	-	-	-	-	-	*nd*
COL-C-6071	12A	III	Single, fine, decorated	425	C_{14}-C_{30}*, C_{32}	C_{24}-C_{32}	C_{23}-C_{29}	-	-	-	-	Beeswax (or plants)
COL-C-6072	12A	III	Single, fine, decorated	22	C_{16}-C_{26}*	C_{16}-C_{28}	-	-	-	-	-	Mixture animal fats and beeswax/plant?
COL-C-6073	12A	III	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
COL-C-6074	12A	III	Single, coarse, undecorated	43	C_{16}-C_{26}*, C_{28}	-	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6075	12A	III	Single, coarse, undecorated	15	C_{16}-C_{30}*, C_{32}	C_{14}-C_{32}	C_{23}-C_{29}	-	-	-	-	Probable modern contamination
COL-C-6076	12A	III	Single, coarse, undecorated	36	C_{16}-C_{30}*	C_{24}-C_{32}	-	-	-	-	-	Plants?
COL-C-6077	7A	II	Single, coarse, undecorated	5	C_{16}-C_{24}*, C_{26}	-	-	-	-	-	-	Probable modern contamination
COL-C-6078	7A	II	Refitted, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6079	7A	II	Single, coarse, undecorated	7	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6080	7A	II	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6081	10A	II	Single, fine, undecorated	7	-	-	-	-	-	-	-	-
COL-C-6082	10A	II	Single, fine, decorated	9	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6083	10A	II	Single, fine, decorated	8	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6084	10A	II	Single, fine, decorated	6	C_{16}-C_{26}*	C_{16}-C_{24}	-	-	-	-	-	Probable modern contamination
COL-C-6085	10A	II	Single, fine, undecorated	600	C_{14}-C_{26}*	C_{24}-C_{32}	C_{23}-C_{29}	-	-	-	-	Mixture animal fats and beeswax?
COL-C-6086	10A	II	Refitted, fine, undecorated	137	C_{14}-C_{26}*	C_{16}-C_{18}	-	-	-24.5	-25.7	-1.2	Mixture ruminant and non-ruminant adipose fats
COL-C-6087	7A	II	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6088	7A	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6089	7A	II	Single, coarse, undecorated	29	C_{16}-C_{26}*	C_{16}-C_{18}	-	-	*nd*	*nd*	*nd*	*nd*
COL-C-6090	7A	II	Single, fine, decorated	9	-	-	-	-	-	-	-	Probable modern contamination
COL-C-6091	7A	II	Single, fine, decorated	102	C_{14}-C_{20}	-	-	-	-	-	-	Probable modern contamination
COL-C-6092	7A	II	Single, fine, decorated	26	C_{14}-C_{30}*	C_{16}-C_{30}	C_{23}-C_{31}	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6093	7A	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6094	7A	II	Refitted, fine, decorated	22	C_{14}-C_{30}*	C_{16}-C_{32}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
COL-C-6095	7A	II	Single, fine, decorated	0	-	-	-	-	-	-	-	-
COL-C-6096	7A	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6097	7A	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6098	7A	II	Single, coarse, undecorated	7	C_{14}-C_{28}*	C_{16}	-	-	-	-	-	Animal fats
COL-C-6099	7A	II	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6100	7A	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6101	7A	II	Single, coarse, undecorated	15	C_{14}-C_{28}*	C_{14}-C_{26}	C_{23}-C_{27}	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6102	7A	II	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
COL-C-6103	7A	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6104	7A	II	Single, fine, decorated	17	-	-	-	-	-	-	-	-
COL-C-6105	1	II	Single, coarse, undecorated	10	-	-	-	-	-	-	-	-
COL-C-6106	1	II	Single, coarse, undecorated	46	C_{14}-C_{30}*	C_{16}-C_{32}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6107	1	II	Single, coarse, undecorated	89	C_{14}-C_{30}*	C_{14}-C_{32}	-	-	-	-	-	-
COL-C-6108	1	II	Single, coarse, undecorated	8	-	-	-	-	-	-	-	-
COL-C-6109	10A	II	Single, fine, decorated	7	-	-	-	-	-	-	-	-
COL-C-6110	10A	II	Single, fine, undecorated	21	C_{14}-C_{26}*	C_{14}-C_{20}	-	-	-	-	-	-

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
COL-C-6111	10A	II	Single, fine, decorated	64	C_{14}-C_{26}*	C_{14}-C_{20}, C_{26}	-	-	-26.9	-29.8	-2.9	Mixture ruminant and non-ruminant adipose fats
COL-C-6113	STA	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6114	21	I	Single, coarse, undecorated	4	C_{16}-C_{26}*	-	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6115	21	I	Single, coarse, undecorated	39	C_{16}-C_{30}*	C_{16}-C_{32}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6116	5	I	Single, fine, decorated	34	C_{14}-C_{30}*	C_{14}-C_{32}	C_{21}-C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6117	5	I	Single, coarse, undecorated	80	C_{13}-C_{26}*	C_{12}-C_{14}	C_{20}-C_{26}*	-	-	-	-	Probable modern contamination
COL-C-6118	3B	I	Refitted, coarse, undecorated	90	C_{14}-C_{30}*	C_{16}-C_{18}, C_{26}-C_{32}	-	-	-25.7	-30.4	-4.7	Mixture dairy and non-ruminant adipose fats
COL-C-6119	3B	I	Refitted, fine, decorated	59	C_{14}-C_{30}*	C_{14}-C_{24}*, C_{26}-C_{32}	C_{22}-C_{29}*, C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6120	3B	I	Single, fine, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6121	3B	I	Single, fine, undecorated	16	C_{16}-C_{28}*	-	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6122	17	I	Single, fine, decorated	218	C_{16}-C_{26}*	C_{16}-C_{18}	-	-	-28.1	-31.0	-2.9	Mixture ruminant and non-ruminant adipose fats
COL-C-6123	17	I	Single, fine, decorated	3	-	-	-	-	-	-	-	-
COL-C-6124	17	I	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6125	17	I	Single, coarse, undecorated	19	C_{16}-C_{26}	C_{16}-C_{18}	-	-	-27.2	-24.9	2.3	Non-ruminant fats
COL-C-6126	17	I	Single, coarse, undecorated	321	C_{15}-C_{22}*, C_{24}-C_{28}	C_{16}-C_{30}	-	-	-27.4	-28.5	-1.2	Mixture ruminant and non-ruminant adipose fats
COL-C-6127	17	I	Single, fine, undecorated	8	-	-	-	-	-	-	-	-
COL-C-6128	17	I	Single, fine, decorated	4	-	-	-	-	-	-	-	-
COL-C-6129	17	I	Refitted, fine, decorated	12	-	-	-	-	-	-	-	-
COL-C-6130	17	I	Single, fine, decorated	2	-	-	-	-	-	-	-	-
COL-C-6131	17	I	Single, fine, decorated	9	-	-	-	-	-	-	-	-
COL-C-6132	17	I	Single, coarse, undecorated	909	C_{14}-C_{30}*	C_{12}-C_{18}	-	-	-28.4	-29.3	-1.0	Mixture ruminant and non-ruminant adipose fats
COL-C-6133	5	I	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6134	5	I	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6135	18A	I	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
COL-C-6136		I	Single, fine, decorated	17	C_{14}-C_{26}*, C_{28}-C_{30}	C_{14}-C_{28}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6137	STA	II	Single, fine, decorated	20	C_{14}-C_{28}*	C_{14}-C_{22}*, C_{24}-C_{32}	-	-	-	-	-	*nd*
COL-C-6138	STA	II	Single, fine, decorated	18	C_{14}-C_{28}*	C_{14}-C_{28}	C_{21}-C_{29}*	-	-	-	-	*nd*
COL-C-6139	STA	II	Single, fine, decorated	13	-	-	-	-	-	-	-	-
COL-C-6140	STA	II	Single, coarse, undecorated	8	C_{14}-C_{28}*, C_{30}	C_{12}-C_{28}	-	-	-	-	-	*nd*
COL-C-6141	STA	II	Single, fine, decorated	16	C_{14}-C_{28}*, C_{30}	C_{14}-C_{30}	-	-	-	-	-	*nd*
COL-C-6142	STA	II	Single, coarse, undecorated	229	C_{14}-C_{30}*	C_{12}-C_{32}	-	-	-26.3	-27.9	-1.7	Mixture ruminant and non-ruminant adipose fats
COL-C-6143	STA	II	Single, fine, undecorated	4	-	-	-	-	-	-	-	-
COL-C-6144	STA	II	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6145	STA	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6146	STA	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6147	STA	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6148	STA	II	Refitted, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6149	STA	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6150	STA	II	Single, fine, undecorated	13	-	-	-	-	-	-	-	-
COL-C-6151	STA	II	Single, coarse, undecorated	42	C_{15}-C_{28}*	C_{16}-C_{18}	-	-	-26.4	-27.6	-1.2	Mixture ruminant and non-ruminant adipose fats
COL-C-6152	STA	II	Single, coarse, undecorated	6	-	-	-	-	-	-	-	-
COL-C-6153	STA	II	Single, coarse, undecorated	6	-	-	-	-	-	-	-	-
COL-C-6154	STA	II	Single, coarse, undecorated	10	C_{14}-C_{26}*, C_{28}	C_{14}-C_{18}	-	-	-	-	-	-
COL-C-6155	STA	II	Refitted, coarse, undecorated	7	-	-	-	-	-	-	-	-
COL-C-6156	STA	II	Refitted, fine, decorated	66	C_{14}-C_{28}*, C_{30}	C_{12}-C_{28}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and plants?
COL-C-6157	STA	II	Single, coarse, undecorated	9	-	-	-	-	-	-	-	-

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
COL-C-6158	STA	II	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
COL-C-6159	STA	II	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6160	STA	II	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
COL-C-6161	25	II	Single, fine, decorated	10	-	-	-	-	-	-	-	-
COL-C-6162	25	II	Single, coarse, undecorated	25	C_{13}-C_{30}*	C_{12}-C_{30}	C_{23}-C_{31}	-	-	-	-	Plants?
COL-C-6163	25	II	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
COL-C-6164	83	II	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6165	83	II	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6166	100	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6167	71	II	Single, fine, decorated	3	-	-	-	-	-	-	-	-
COL-C-6168	71	II	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6169	71	II	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6170	65	II	Single, coarse, undecorated	11	C_{14}-C_{30}*	C_{14}-C_{30}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6171	65	II	Single, coarse, undecorated	4	C_{16}-C_{26}*	C_{16}-C_{28}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6172	65	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6173	110	III	Single, fine, decorated	1	-	-	-	-	-	-	-	-
COL-C-6174	110	III	Refitted, coarse, undecorated	333	C_{14}-C_{30}	C_{18}-C_{32}	-	-	-26.5	-28.1	-1.6	Mixture ruminant and non-ruminant adipose fats
COL-C-6175	47	III	Single, fine, decorated	12	C_{16}-C_{28}*	C_{16}-C_{32}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
COL-C-6176	47	III	Single, fine, decorated	10	C_{14}-C_{26}*	C_{14}-C_{26}	-	-	-	-	-	nd
COL-C-6177	47	III	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6178	47	III	Refitted, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6179	62	III	Refitted, coarse, undecorated	5	-	-	-	-	-	-	-	-
COL-C-6180	62	III	Refitted, fine, decorated	7	C_{14}-C_{28}*	C_{14}-C_{20}	-	-	-	-	-	-
COL-C-6181	62	III	Single, fine, decorated	2	-	-	-	-	-	-	-	-
COL-C-6182	62	III	Single, fine, decorated	2	-	-	-	-	-	-	-	-
COL-C-6183	153	III	Single, fine, decorated	4	-	-	-	-	-	-	-	-
COL-C-6184	153	III	Single, fine, decorated	49	C_{14}-C_{28}*	C_{12}-C_{24}*, C_{26}-C_{30}	C_{23}-C_{31}	-	-	-	-	Mixture animal fats and beeswax?
COL-C-6185	153	III	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
COL-C-6186	153	III	Single, coarse, undecorated	5	C_{16}-C_{28}*	C_{18}-C_{30}	C_{25}-C_{29}	-	-	-	-	*nd*
COL-C-6187	62	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6188	62	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6189	F1	II	Single, fine, decorated	14	C_{16}-C_{28}*	C_{18}-C_{28}	-	-	-	-	-	*nd*
COL-C-6190	F1	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6191	F1	II	Single, coarse, undecorated	31	C_{16}-C_{24}*, C_{26}	-	-	-	-	-	-	*nd*
COL-C-6192	F1	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6193	F1	II	Single, coarse, undecorated	9	C_{16}-C_{18}	C_{18}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6194	F1	II	Single, fine, decorated	30	C_{16}-C_{30}*	C_{24}-C_{32}	C_{25}-C_{31}	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6195	F1	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6196	F1	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
COL-C-6197	F1	II	Single, fine, decorated	16	C_{16}-C_{28}*	C_{16}-C_{30}	C_{27}-C_{31}	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6198	F1	II	Single, fine, decorated	34	C_{16}-C_{30}	C_{24}-C_{32}	C_{25}-C_{31}	-	-	-	-	Beeswax (or plants)
COL-C-6199	F2	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6200	F2	II	Single, coarse, undecorated	9	C_{14}-C_{26}*, C_{28}	C_{14}-C_{30}	C_{21}-C_{29}	-	-	-	-	*nd*
COL-C-6201	F2	II	Refitted, fine, decorated	12	-	-	-	-	-	-	-	-
COL-C-6202	F2	II	Single, fine, decorated	68	C_{14}-C_{26}*, C_{28}	C_{14}-C_{30}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6203	F2	II	Refitted, fine, decorated	13	C_{14}-C_{26}*, C_{28}	C_{14}-C_{30}	-	-	*nd*	*nd*	*nd*	Animal fats

Sherd #	Pit	Phase	Description	C° (µg.g^{-1})	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
COL-C-6204	F2	II	Single, coarse, undecorated	12	C_{14}-C_{26}*, C_{28}	C_{16}-C_{18}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6205	F2	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6206	F2	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6207	F2	II	Single, fine, decorated	8	-	-	-	-	-	-	-	-
COL-C-6208	F2	II	Single, fine, decorated	10	C_{15}-C_{26}*	C_{14}-C_{22}	-	-	*nd*	*nd*	*nd*	Animal fats
COL-C-6209	F3	II	Refitted, fine, decorated	8	C_{15}-C_{30}*	C_{16}-C_{32}	-	-	-	-	-	-
COL-C-6210	F3	II	Refitted, coarse, undecorated	1	-	-	-	-	-	-	-	-
COL-C-6211	F3	II	Refitted, coarse, undecorated	0	-	-	-	-	-	-	-	-
COL-C-6212	F3	II	Single, coarse, undecorated	7	C_{16}-C_{28}*	C_{18}, C_{26}	-	-	-	-	-	*nd*
COL-C-6213	F3	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-

Appendix 6-15: Potsherds characteristics and results of ORA at the site of Ensisheim "Ratfeld". The codes are analogous to those given in Appendix 6.5.

Sherd #	Pit	Phase	Description	C° (ug.g^{-1})	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ENS-C-5911	9	II	Single, coarse, undecorated	27	C_{14}-C_{26}	C_{26}-C_{32}	-	-	-28.1	-29.5	-1.3	Mixture ruminant and non-ruminant adipose fats
ENS-C-5912	9	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5913	9	II	Single, coarse, undecorated	1177	C_{14}-C_{28}*	C_{14}-C_{20}	-	-	-27.3	-30.9	-3.6	Mixture dairy and non-ruminant adipose fats
ENS-C-5914	9	II	Refitted, fine, decorated	132	C_{14}-C_{30}*	C_{24}-C_{32}	C_{23}-C_{31}	-	-25.2	-28.1	-2.9	Mixture ruminant, non-ruminant adipose fats, beeswax?
ENS-C-5915	9	II	Single, coarse, undecorated	771	C_{14}-C_{28}	C_{14}-C_{28}	-	-	-26.4	-29.6	-3.2	-
ENS-C-5916	9	II	Single, coarse, undecorated	765	C_{12}-C_{28}	-	-	-	-26.9	-29.8	-2.9	Mixture ruminant and non-ruminant adipose fats
ENS-C-5917	9	II	Single, coarse, undecorated	168	C_{14}-C_{30}*	C_{14}-C_{26}*, C_{28}-C_{32}	-	-	-27.0	-31.1	-4.1	Mixture dairy, non-ruminant adipose fats and beeswax?
ENS-C-5918	9	II	Single, fine, decorated	7	-	-	-	-	-	-	-	-
ENS-C-5919	18	II	Single, fine, decorated	102	C_{14}-C_{28}	C_{16}-C_{26}*, C_{28}-C_{30}	C_{25}-C_{31}	-	-28.7	-32.6	-3.8	Dairy fats
ENS-C-5920	18	II	Single, fine, decorated	2	-	-	-	-	-	-	-	-
ENS-C-5921	18	II	Single, coarse, undecorated	41	C_{14}-C_{26}*, C_{28}	C_{14}-C_{24}	-	-	-28.9	-31.5	-2.6	Ruminant adipose fats
ENS-C-5922	18	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5923	18	II	Single, coarse, undecorated	9	-	-	-	-	-	-	-	-
ENS-C-5924	18	II	Single, coarse, undecorated	140	C_{14}-C_{28}*	-	-	-	-26.8	-27.1	-0.3	Mixture ruminant and non-ruminant adipose fats
ENS-C-5925	18	II	Fine, undecorated	56	-	-	-	-	-	-	-	-
ENS-C-5926	18	II	Single, fine, decorated	7	-	-	-	-	-	-	-	-
ENS-C-5927	18	II	Single, fine, decorated	3	-	-	-	-	-	-	-	-
ENS-C-5928	28	II	Single, fine, decorated	74	C_{14}-C_{28}*, C_{30}	C_{24}-C_{32}	C_{23}-C_{31}	-	-25.3	-28.9	-3.6	Mixture dairy, non-ruminant fats, plant/beeswax?
ENS-C-5929	28	II	Single, fine, decorated	96	C_{14}-C_{26}*, C_{28}-C_{30}	C_{14}-C_{26}*, C_{28}-C_{30}	C_{23}-C_{31}	-	-27.7	-31.4	-3.8	Mixture dairy, non-ruminant fats, plant/beeswax?
ENS-C-5930	28	II	Single, fine, decorated	37	C_{14}-C_{30}*	C_{14}-C_{26}*, C_{28}	C_{22}-C_{33}*	-	-25.5	-29.9	-4.4	Mixture dairy, non-ruminant adipose fats and plant?
ENS-C-5931	28	II	Refitted, fine, decorated	5	-	-	-	-	-	-	-	-
ENS-C-5932	28	II	Single, coarse, decorated	22	C_{14}-C_{28}	C_{14}-C_{18}	-	-	-26.4	-30.2	-3.8	Mixture dairy and non-ruminant adipose fats
ENS-C-5933	28	II	Single, fine, decorated	38	C_{14}-C_{29}*	C_{14}-C_{28}	-	-	-28.2	-32.9	-4.7	Dairy fats
ENS-C-5934	28	II	Single, coarse, undecorated	1647	C_{12}-C_{26}*	C_{24}-C_{32}	-	-	-26.2	-29.7	-3.5	Mixture dairy and non-ruminant adipose fats
ENS-C-5935	28	II	Single, coarse, undecorated	805	C_{14}-C_{28}*, C_{30}	C_{24}-C_{32}	-	-	-27.8	-30.0	-2.2	Mixture ruminant and non-ruminant adipose fats
ENS-C-5936	28	II	Single, coarse, undecorated	11	C_{16}-C_{28}*, C_{30}	C_{14}-C_{32}	C_{23}-C_{31}	-	-	-	-	Animal fats
ENS-C-5937	28	II	Single, coarse, undecorated	13	C_{15}-C_{30}*	C_{14}-C_{30}	C_{17}-C_{27}	-	-	-	-	*nd*
ENS-C-5938	28	II	Single, coarse, undecorated	94	C_{14}-C_{28}*	C_{14}-C_{30}	C_{27}-C_{31}	-	-26.5	-27.9	-1.4	Mixture ruminant and non-ruminant adipose fats

Sherd #	Pit	Phase	Description	C° (ug.g^{-1})	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ENS-C-5939	28	II	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ENS-C-5940	28	II	Single, coarse, undecorated	2082	C_{14}-C_{24}	C_{16}-C_{18}	-	-	-28.7	-30.9	-2.2	Ruminant fats
ENS-C-5941	46	II	Single, fine, decorated	116	C_{16}-C_{26}*, C_{28}-C_{30}	C_{16}-C_{32}	C_{25}-C_{31}	-	-24.7	-27.2	-2.6	Mixture ruminant, non-ruminant adipose fats, beeswax?
ENS-C-5942	46	II	Single, fine, decorated	49	C_{15}-C_{28}*, C_{30}	C_{16}-C_{32}	C_{25}-C_{31}	-	-29.1	-29.9	-0.8	Mixture ruminant and non-ruminant adipose fats
ENS-C-5943	46	II	Single, coarse, undecorated	53	C_{14}-C_{26}*, C_{28}	C_{14}-C_{20}	-	-	-26.4	-28.9	-2.4	Mixture ruminant and non-ruminant adipose fats
ENS-C-5944	46	II	Single, coarse, undecorated	22	C_{14}-C_{30}*	C_{14}-C_{28}	-	-	-27.0	-30.4	-3.5	Mixture dairy and non-ruminant adipose fats
ENS-C-5945	46	II	Single, coarse, undecorated	12	C_{14}-C_{28}*	C_{14}-C_{28}	-	-	-	-	-	nd
ENS-C-5946	18	II	Single, coarse, undecorated	401	C_{14}-C_{28}*	C_{26}-C_{30}	-	-	-28.6	-31.3	-2.7	Ruminant adipose fats
ENS-C-5947	18	II	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5948	31	III	Single, coarse, undecorated	7	-	-	-	-	-	-	-	-
ENS-C-5949	31	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ENS-C-5950	31	III	Single, fine, decorated	21	C_{14}-C_{26}*, C_{28}	C_{14}-C_{30}	C_{23}-C_{31}	-	-27.1	-31.7	-4.6	Mixture dairy and non-ruminant adipose fats
ENS-C-5951	31	III	Single, fine, decorated	9	C_{14}-C_{26}*	C_{14}-C_{28}	C_{23}-C_{31}	-	-25.2	-26.4	-1.2	Mixture ruminant and non-ruminant adipose fats
ENS-C-5952	31	III	Single, fine, decorated	170	C_{14}-C_{24}*, C_{26}-C_{28}	C_{18}-C_{32}	C_{23}-C_{31}	-	-25.8	-28.3	-2.5	Mixture ruminant, non-ruminant adipose fats, beeswax
ENS-C-5953	31	III	Single, fine, decorated	76	C_{14}-C_{18}*, C_{30}	C_{14}-C_{32}	-	-	-27.3	-30.2	-2.9	Mixture ruminant and non-ruminant adipose fats
ENS-C-5954	31	III	Single, fine, decorated	202	C_{14}-C_{26}*, C_{28}	C_{12}-C_{30}	C_{25}-C_{31}	-	-27.6	-30.7	-3.2	Mixture dairy and non-ruminant adipose fats
ENS-C-5955	31	III	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ENS-C-5956	31	III	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5957	31	III	Single, coarse, undecorated	31	C_{14}-C_{26}	-	-	-	-	-	-	Modern contamination
ENS-C-5958	31	III	Single, coarse, undecorated	15	-	-	-	-	-	-	-	-
ENS-C-5959	31	III	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
ENS-C-5960	31	III	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5961	31	III	Single, coarse, undecorated	348	C_{14}-C_{28}*	-	-	-	-25.2	-28.2	-3.1	Mixture dairy and non-ruminant adipose fats
ENS-C-5962	31	III	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
ENS-C-5963	31	III	Refitted, fine, decorated	73	C_{14}-C_{28}*, C_{30}	C_{14}-C_{28}	-	-	-26.3	-27.6	-1.3	Mixture ruminant and non-ruminant adipose fats
ENS-C-5964	31	III	Single, fine, decorated	9	-	-	-	-	-	-	-	-
ENS-C-5965	31	III	Single, fine, decorated	30	C_{14}-C_{26}*, C_{28}	C_{14}-C_{32}	-	-	-26.7	-30.3	-3.6	Mixture dairy and non-ruminant adipose fats
ENS-C-5966	31	III	Refitted, fine, decorated	60	C_{12}-C_{26}*, C_{28}	C_{12}-C_{26}	-	-	-	-	-	*nd*
ENS-C-5967	31	III	Single, fine, decorated	5	-	-	-	-	-	-	-	-
ENS-C-5968	31	III	Single, fine, decorated	31	C_{14}-C_{30}*	C_{14}-C_{32}	C_{27}-C_{31}	-	-26.5	-29.6	-3.1	Mixture dairy and non-ruminant adipose fats
ENS-C-5969	31	III	Single, fine, decorated	99	C_{14}-C_{26}*, C_{28}	C_{14}-C_{24}*, C_{26}-C_{30}	C_{25}-C_{31}	-	-26.6	-29.8	-3.2	Mixture dairy and non-ruminant adipose fats
ENS-C-5970	31	III	Single, fine, decorated	144	C_{14}-C_{26}*, C_{28}	C_{14}-C_{26}	C_{29}-C_{31}	-	-25.7	-29.7	-4.0	Mixture dairy and non-ruminant adipose fats
ENS-C-5971	31	III	Single, fine, decorated	40	C_{14}-C_{28}*, C_{30}	C_{14}-C_{32}	C_{25}-C_{31}	-	-26.2	-29.4	-3.3	Mixture dairy and non-ruminant adipose fats
ENS-C-5972	31	III	Single, fine, decorated	106	C_{14}-C_{28}*, C_{30}	C_{16}-C_{32}	C_{25}-C_{31}	-	-27.2	-29.8	-2.6	Mixture ruminant and non-ruminant adipose fats
ENS-C-5973	20	III	Refitted, fine, decorated	243	C_{12}-C_{26}*, C_{28}	C_{14}-C_{32}	C_{32}-C_{31}	-	-26.1	-27.6	-1.6	Mixture ruminant, non-ruminant adipose fats, beeswax
ENS-C-5974	50	III	Single, fine, decorated	11	C_{12}-C_{18}	C_{14}-C_{18}	-	-	-	-	-	-
ENS-C-5975	50	III	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
ENS-C-5976	24	III	Single, fine, decorated	81	C_{14}-C_{28}	C_{14}-C_{28}	C_{27}-C_{29}	-	-25.6	-28.0	-2.3	Mixture ruminant, non-ruminant adipose fats, beeswax
ENS-C-5977	24	III	Single, coarse, undecorated	6	-	-	-	-	-	-	-	-
ENS-C-5978	24	III	Single, coarse, undecorated	648	C_{14}-C_{24}*	C_{12}-C_{14}, C_{18}	-	-	-27.1	-28.9	-1.8	Mixture ruminant and non-ruminant adipose fats
ENS-C-5979	24	III	Single, coarse, undecorated	21	-	-	-	-	-	-	-	*nd*
ENS-C-5980	24	III	Single, coarse, undecorated	27	C_{14}-C_{28}*	C_{14}-C_{28}	C_{27}-C_{31}	K	-26.6	-26.1	0.5	Non-ruminant adipose fats
ENS-C-5981	69	III	Single, fine, decorated	78	C_{14}-C_{26}*, C_{28}	C_{14}-C_{32}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plant)
ENS-C-5982	11	III	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
ENS-C-5983	12	IV ?	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
ENS-C-5984	57	IV ?	Refitted, fine, decorated	32	C_{14}-C_{28}*, C_{30}	C_{14}-C_{28}	-	-	-	-	-	*nd*

Sherd #	Pit	Phase	Description	C^o ($ug.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
ENS-C-5985	5	IV ?	Single, fine, decorated	110	C_{14}-C_{26}*, C_{28}	C_{14}-C_{28}	-	-	-24.0	-24.9	-0.8	Mixture ruminant and non-ruminant adipose fats
ENS-C-5986	5	IV ?	Single, coarse, undecorated	965	C_{14}-C_{24}*	C_{14}-C_{18}	-	-	-28.3	-30.9	-2.6	Mixture dairy and non-ruminant adipose fats
ENS-C-5987	73	IV ?	Single, fine, decorated	26	C_{14}-C_{22}*, C_{24}	C_{14}-C_{22}	-	-	-	-	-	*nd*
ENS-C-5988	73	IV ?	Single, coarse, undecorated	12	-	-	-	-	-	-	-	*nd*
ENS-C-5989	36	IV	Single, coarse, undecorated	9	-	-	-	-	-	-	-	*nd*
ENS-C-5990	36	IV	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
ENS-C-5991	36	IV	Single, coarse, undecorated	30	C_{14}-C_{24}*, C_{26}	C_{14}-C_{28}	-	-	-26.3	-30.8	-4.5	Mixture dairy and non-ruminant adipose fats
ENS-C-5992	36	IV	Single, coarse, undecorated	5	-	-	-	-	-	-	-	-
ENS-C-5993	36	IV	Single, coarse, undecorated	$_{14}$	C_{14}-C_{24}*, C_{26}	C_{12}-C_{18}, C_{26}	-	-	-27.3	-30.3	-3.0	Mixture ruminant and non-ruminant adipose fats
ENS-C-5994	36	IV	Single, fine, decorated	64	C_{14}-C_{26}*	C_{14}-C_{28}	-	-	-27.4	-30.4	-3.0	Mixture dairy and non-ruminant adipose fats
ENS-C-5995	36	IV	Single, fine, decorated	11	-	-	-	-	-26.7	-30.3	-3.6	Mixture dairy and non-ruminant adipose fats
ENS-C-5996	36	IV	Single, fine, decorated	150	C_{14}-C_{28}*, C_{30}	C_{14}-C_{30}	C_{23}-C_{31}	-	-27.4	-29.7	-2.3	Mixture ruminant and non-ruminant adipose fats
ENS-C-5997	36	IV	Single, fine, decorated	105	C_{12}-C_{35}*, C_{28}-C_{30}	C_{14}-C_{26}*, C_{28}-C_{30}	C_{17}-C_{31}	-	-26.1	-28.3	-2.2	Mixture ruminant and non-ruminant adipose fats
ENS-C-5998	36	IV	Single, fine, decorated	27	C_{14}-C_{24}*, C_{26}	C_{14}-C_{26}	-	-	-	-	-	*nd*
ENS-C-5999	36	IV	Single, fine, decorated	23	C_{14}-C_{26}*, C_{28}	C_{14}-C_{24}*, C_{26}-C_{28}	-	-	-	-	-	*nd*
ENS-C-6000	36	IV	Single, fine, decorated	22	C_{14}-C_{26}*, C_{28}	C_{12}-C_{24}*, C_{26}-C_{30}	-	-	-	-	-	*nd*
ENS-C-6001	36	IV	Single, fine, undecorated	5	-	-	-	-	-	-	-	-
ENS-C-6002	36	IV	Single, fine, undecorated	116	C_{14}-C_{28}*, C_{30}	C_{14}-C_{32}	C_{25}-C_{31}	-	-27.0	-30.9	-3.9	Mixture dairy, non-ruminant fats, plant/beeswax
ENS-C-6003	36	IV	Refitted, fine, undecorated	32	C_{14}-C_{28}*	C_{12}-C_{26}*, C_{28}-C_{30}	C_{27}-C_{31}	-	-	-	-	*nd*
ENS-C-6004	36	IV	Single, fine, undecorated	86	C_{12}-C_{26}*, C_{32}	C_{12}-C_{24}*, C_{26}-C_{32}	-	-	-27.9	-29.9	-2.0	Mixture ruminant and non-ruminant adipose fats
ENS-C-6005	36	IV	Single, fine, undecorated	117	C_{14}-C_{24}, C_{26}-C_{32}	C_{24}-C_{34}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plant)
ENS-C-6006	36	IV	Single, fine, undecorated	4	-	-	-	-	-	-	-	-
ENS-C-6007	36	IV	Single, fine, undecorated	9	-	-	-	-	-	-	-	-
ENS-C-6008	36	IV	Single, coarse, undecorated	364	C_{14}-C_{24}*, C_{26}-C_{30}	C_{24}-C_{32}	C_{23}-C_{31}	-	-	-	-	Beeswax (or plant)
ENS-C-6009	36	IV	Single, coarse, undecorated	464	C_{14}-C_{26}*	C_{20}-C_{28}	C_{27}-C_{33}	-	-26.1	-26.2	-0.1	Non-ruminant adipose fats
ENS-C-6010	36	IV	Single, coarse, undecorated	6	-	-	-	-	-	-	-	-
ENS-C-6011	56	IV	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-

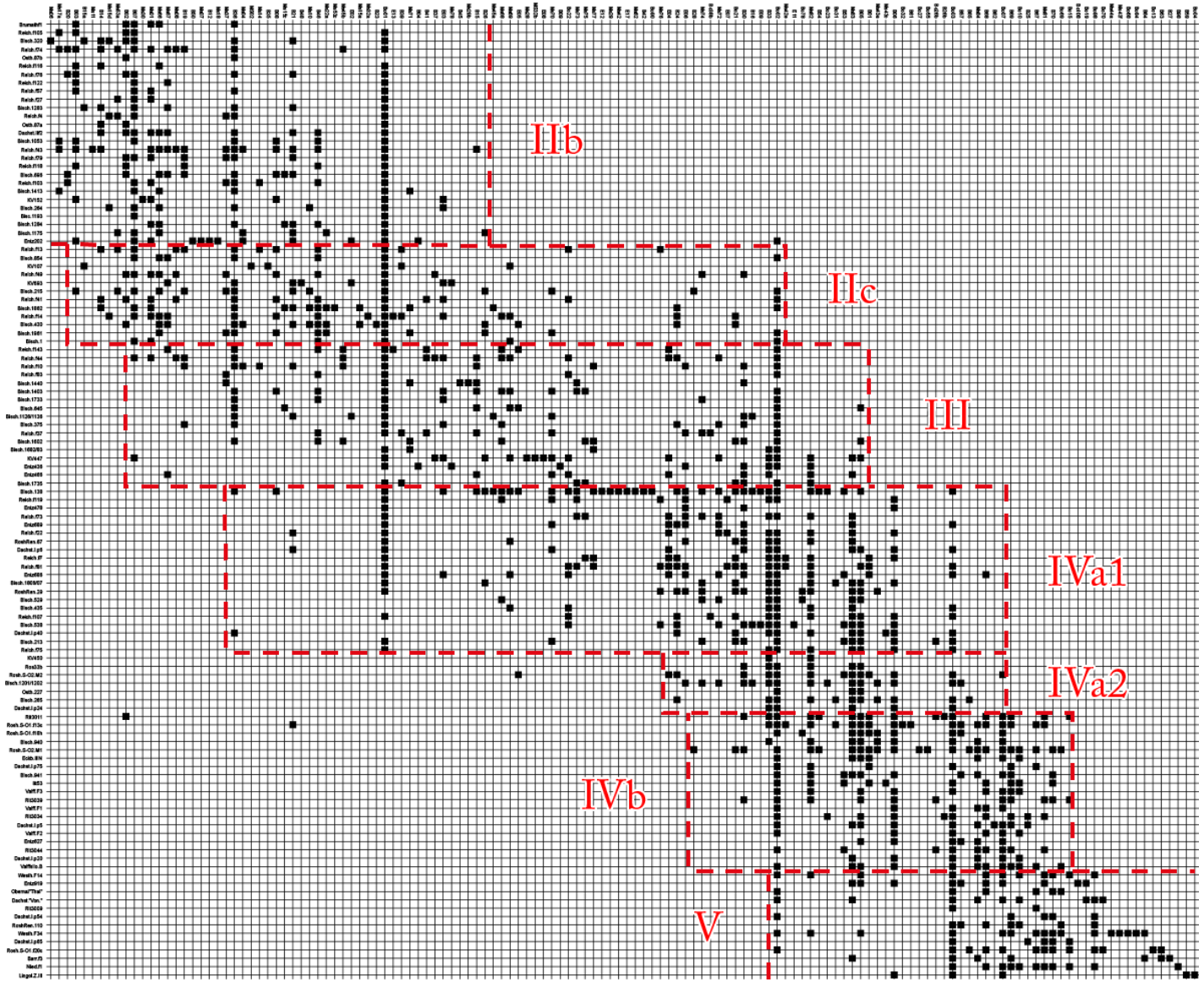
Appendix 6-16: Potsherds characteristics and results of ORA at the site of Sierentz “Sandgrube, Tiergarten”. The codes are analogous to those given in Appendix 6.5.

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
SIE-C-5341	20	IV B	Single, coarse, undecorated	112	C_{14}-C_{28}	C_{16}-C_{24}	-	-	-27.7	-30.1	-2.5	Mixture ruminant and non-ruminant adipose fats
SIE-C-5342	21	IV B	Single, coarse, undecorated	438	C_{14}-C_{28}	C_{16}-C_{28}	C_{25}-C_{29}	-	-29.1	-31.8	-2.8	Mixture ruminant fats and plant?
SIE-C-5343	21	IV B	Single, fine, undecorated	243	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-28.4	-31.2	-2.8	Ruminant adipose fats
SIE-C-5344	21	IV B	Single, coarse, undecorated	1311	C_{14}-C_{28}	C_{16}-C_{18}	-	K	-27.5	-28.8	-1.3	Mixture ruminant and non-ruminant adipose fats
SIE-C-5345	21	IV B	Single, coarse, undecorated	178	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-27.7	-31.7	-4.0	Mixture dairy and non-ruminant adipose fats
SIE-C-5346	21	IV B	Single, coarse, undecorated	195	C_{14}-C_{30}	C_{16}-C_{30}	C_{25}	-	-28.1	-31.2	-3.1	Mixture dairy and non-ruminant adipose fats
SIE-C-5347	21	IV B	Single, coarse, decorated	0	-	-	-	-	-	-	-	-
SIE-C-5348	21	IV B	Single, coarse, decorated	0	-	-	-	-	-	-	-	-
SIE-C-5349	21	IV B	Refitted, coarse, decorated	22	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-	-	-	*nd*
SIE-C-5350	21	IV B	Single, fine, undecorated	25	C_{14}-C_{30}	C_{16}-C_{30}	C_{25}-C_{27}	-	-	-	-	Mixture animal fats and plant?
SIE-C-5351	21	IV B	Single, fine, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5352	21	IV B	Single, coarse, undecorated	341	C_{14}-C_{28}	C_{16}-C_{30}	C_{25}-C_{27}	-	-28.2	-31.2	-2.9	Mixture ruminant and non-ruminant adipose fats

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
SIE-C-5353	21	IV B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5354	22	IV B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5355	22	IV B	Single, fine, undecorated	126	C_{14}-C_{28}	C_{16}-C_{26}	-	-	-27.0	-30.1	-3.1	Mixture ruminant and non-ruminant adipose fats
SIE-C-5356	22	IV B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5357	22	IV B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5358	22	IV B	Single, coarse, undecorated	41	C_{16}, C_{24}-C_{30}	C_{20}-C_{30}	C_{25}-C_{31}	-	-	-	-	Beeswax?
SIE-C-5359	22	IV B	Single, coarse, undecorated	208	C_{16}, C_{22}-C_{30}	C_{14}-C_{30}	C_{25}-C_{31}	-	-	-	-	Beeswax?
SIE-C-5360	22	IV B	Single, coarse, undecorated	8	C_{14}-C_{30}	C_{16}-C_{26}	-	-	-	-	-	*nd*
SIE-C-5361	22	IV B	Single, coarse, undecorated	5	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-	-	-	*nd*
SIE-C-5362	23	IV B	Single, coarse, undecorated	807	C_{14}-C_{28}	C_{16}-C_{18}	-	-	-27.5	-31.7	-4.2	Mixture dairy and non-ruminant adipose fats
SIE-C-5363	23	IV B	Single, coarse, undecorated	86	C_{14}-C_{28}	C_{16}-C_{26}	-	-	-29.2	-33.6	-4.4	Dairy fats
SIE-C-5364	23	IV B	Single, coarse, undecorated	1169	-	-	-	-	-27.9	-29.8	-1.9	Mixture ruminant and non-ruminant adipose fats
SIE-C-5365	26	IV A	Single, coarse, undecorated	62	C_{14}-C_{28}	$C1_6$-C_{28}	-	-	-27.5	-30.5	-3.0	Mixture ruminant and non-ruminant adipose fats
SIE-C-5366	26	IV A	Refitted, coarse, undecorated	99	-	-	-	-	-	-	-	*nd*
SIE-C-5367	26	IV A	Single, coarse, undecorated	13	-	-	-	-	-	-	-	*nd*
SIE-C-5368	26	IV A	Single, coarse, undecorated	5	-	-	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5369	26	IV A	Single, coarse, undecorated	6	-	-	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5370	26	IV A	Refitted, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5371	26	IV A	Single, coarse, undecorated	437	C_{14}-C_{26}	-	-	-	-26.8	-30.8	-4.0	Mixture dairy and non-ruminant adipose fats
SIE-C-5372	26	IV A	Single, coarse, undecorated	341	C_{14}-C_{28}	C_{16}-C_{18}	-	-	-29.5	-32.7	-3.2	Mixture ruminant and non-ruminant adipose fats
SIE-C-5373	26	IV A	Single, coarse, undecorated	149	C_{14}-C_{28}	-	-	-	-27.9	-30.2	-2.3	Mixture ruminant and non-ruminant adipose fats
SIE-C-5374	28	IV A	Single, coarse, undecorated	913	C_{14}-C_{28}	C_{16}-C_{26}	-	-	-27.9	-32.7	-4.7	Dairy fats
SIE-C-5375	28	IV A	Single, coarse, undecorated	106	C_{14}-C_{30}	C_{16}-C_{30}	-	-	-27.9	-30.1	-2.2	Mixture ruminant and non-ruminant adipose fats
SIE-C-5376	28	IV A	Single, coarse, undecorated	22	-	-	-	-	-	-	-	*nd*
SIE-C-5377	28	IV A	Single, coarse, undecorated	11	C_{14}-C_{28}	C_{16}-C_{30}	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5378	28	IV A	Single, coarse, undecorated	407	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-27.1	-29.8	-2.7	Mixture ruminant and non-ruminant adipose fats
SIE-C-5379	26	IV A	Single, coarse, undecorated	7	-	-	-	-	-	-	-	*nd*
SIE-C-5380	26	IV A	Single, coarse, undecorated	2494	C_{14}-C_{24}	C_{16}-C_{18}	-	-	-27.0	-28.1	-1.1	Mixture ruminant and non-ruminant adipose fats
SIE-C-5381	26	IV A	Single, coarse, undecorated	215	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-27.0	-30.4	-3.5	Mixture dairy and non-ruminant adipose fats
SIE-C-5382	22	IV A	Refitted, fine, decorated	503	C_{14}-C_{28}	C_{22}-C_{26}	C_{25}-C_{27}	-	-	-	-	Beeswax?
SIE-C-5383	26/28	IV A	Refitted, fine, decorated	250	C_{14}-C_{28}*	C_{14}-C_{30}	C_{25}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5384	26/28	IV A	Refitted, fine, decorated	207	C_{14}-C_{30}*	C_{16}-C_{32}*	C_{25}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5385	26/28	IV A	Single, fine, decorated	178	C_{14}-C_{26}	C_{14}-C_{30}	C_{27}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5386	26/28	IV A	Single, fine, decorated	95	C_{14}-C_{28}	C_{14}-C_{28}	C_{27}-C_{29}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5387	26/28	IV A	Single, fine, decorated	36	C_{14}-C_{28}	C_{16}-C_{28}	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5388	26/28	IV A	Refitted, fine, decorated	91	C_{14}-C_{28}	C_{16}-C_{28}	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5389	26/28	IV A	Single, fine, decorated	0	-	-	-	-	-	-	-	-
SIE-C-5390	26/28	IV A	Single, fine, decorated	41	C_{14}-C_{28}	C_{16}-C_{18}	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5391	26/28	IV A	Refitted, fine, decorated	34	C_{14}-C_{28}	C_{16}-C_{18}	-	-	-	-	-	*nd*
SIE-C-5392	26/28	IV A	Single, fine, decorated	74	C_{14}-C_{28}	-	-	-	-28.7	-31.9	-3.1	Mixture dairy and non-ruminant adipose fats
SIE-C-5393	26/28	IV A	Single, fine, decorated	152	C_{14}-C_{28}	C_{16}-C_{28}	C_{27}-C_{29}	-	-26.3	-30.0	-3.7	Mixture dairy and non-ruminant adipose fats
SIE-C-5394	26/28	IV A	Single, fine, decorated	173	C_{14}-C_{28}	C_{16}-C_{28}	C_{27}-C_{30}	-	-28.0	-31.1	-3.1	Mixture dairy and non-ruminant adipose fats
SIE-C-5395	26/28	IV A	Single, fine, decorated	47	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-26.6	-28.6	-2.0	Mixture ruminant and non-ruminant adipose fats
SIE-C-5396	26/28	IV A	Single, fine, decorated	22	C_{14}-C_{26}	C_{16}-C_{26}	-	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5397	26/28	IV A	Single, fine, decorated	63	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-23.5	-28.3	-4.8	Mixture dairy and non-ruminant adipose fats
SIE-C-5398	26/28	IV A	Refitted, fine, decorated	74	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-26.2	-26.8	-0.6	Mixture ruminant and non-ruminant adipose fats

Sherd #	Pit	Phase	Description	C^o ($\mu g.g^{-1}$)	Fatty acids	Alkanols	Alkanes	Other	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
SIE-C-5399	26/28	IV A	Single, fine, decorated	102	C_{14}-C_{28}	C_{16}-C_{28}	-	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5400	26/28	IV A	Refitted, fine, decorated	20	C_{14}-C_{28}	C_{16}-C_{28}	-	-	-	-	-	*nd*
SIE-C-5401	26/28	IV A	Single, coarse, undecorated	302	C_{14}-C_{30}	C_{14}-C_{18}	-	-	-29.0	-31.3	-2.3	Ruminant adipose fats
SIE-C-5402	26/28	IV A	Refitted, coarse, undecorated	33	C_{14}-C_{30}	-	-	-	-27.3	-29.9	-2.6	Mixture ruminant and non-ruminant adipose fats
SIE-C-5403	26/28	IV A	Single, coarse, undecorated	233	C_{14}-C_{30}	C_{16}-C_{30}	C_{25}-C_{31}	-	-27.0	-28.1	-1.1	Mixture ruminant and non-ruminant adipose fats
SIE-C-5404	26/28	IV A	Single, coarse, undecorated	34	C_{14}-C_{30}	-	-	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5405	26/28	IV A	Single, fine, undecorated	88	C_{14}-C_{30}	C_{16}-C_{32}	-	-	-28.2	-31.6	-3.4	Mixture dairy and non-ruminant adipose fats
SIE-C-5406	1	IV A	Single, coarse, undecorated	241	C_{14}-C_{30}	C_{16}-C_{30}	C_{25}-C_{33}	-	*nd*	*nd*	*nd*	Mixture animal fats and beeswax/plants
SIE-C-5407	1	IV A	Single, coarse, undecorated	41	C_{14}-C_{30}	C_{16}-C_{30}	C_{25}-C_{29}	-	-	-	-	*nd*
SIE-C-5408	1	IV A	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5409	2	IV A	Refitted, coarse, undecorated	191	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-27.2	-29.8	-2.6	Mixture ruminant and non-ruminant adipose fats
SIE-C-5410	2	IV A	Single, coarse, undecorated	21	C_{14}-C_{30}	C_{16}-C_{18}	-	-	-27.5	-31.3	-3.7	Mixture dairy and non-ruminant adipose fats
SIE-C-5411	2	IV A	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5412	3	IV B	Single, coarse, undecorated	7	-	-	-	-	-	-	-	-
SIE-C-5413	3	IV B	Single, coarse, undecorated	739	C_{14}-C_{22}, C_{21}	C_{16}-C_{18}	-	-	-30.9	-33.4	-2.5	Ruminant adipose fats
SIE-C-5414	3	IV B	Single, coarse, undecorated	7	-	-	-	-	-	-	-	*nd*
SIE-C-5415	3	IV B	Single, coarse, undecorated	5	-	-	-	-	-	-	-	*nd*
SIE-C-5416	3	IV B	Single, coarse, undecorated	984	C_{14}-C_{30}	C_{16}-C_{26}	-	-	-27.8	-31.7	-3.9	Mixture dairy and non-ruminant adipose fats
SIE-C-5417	3	IV B	Single, coarse, undecorated	646	C_{14}-C_{28}	C_{16}-C_{26}	-	-	-28.8	-30.2	-1.4	Ruminant adipose fats
SIE-C-5418	3	IV B	Single, coarse, undecorated	495	C_{14}-C_{24}	C_{16}-C_{18}	-	-	-27.9	-29.4	-1.5	Mixture ruminant and non-ruminant adipose fats
SIE-C-5419	7/8	IV B	Single, coarse, undecorated	1	-	-	-	-	-	-	-	-
SIE-C-5420	7/8	IV B	Single, coarse, undecorated	281	C_{14}-C_{30}	-	-	-	-27.5	-29.0	-1.4	Mixture ruminant and non-ruminant adipose fats
SIE-C-5421	7	IV B	Single, coarse, undecorated	0	-	-	-	-	-	-	-	-
SIE-C-5422	7	IV B	Refitted, coarse, undecorated	166	C_{14}-C_{30}	C_{24}-C_{32}	C_{27}-C_{31}	-	-	-	-	Beeswax?
SIE-C-5423	7	IV B	Single, coarse, undecorated	4	-	-	-	-	-	-	-	-
SIE-C-5424	9	IV B	Single, coarse, undecorated	615	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-27.2	-29.4	-2.2	Mixture ruminant and non-ruminant adipose fats
SIE-C-5425	11	IV A	Single, coarse, undecorated	19	C_{14}-C_{28}	C_{16}-C_{26}	-	-	-	-	-	*nd*
SIE-C-5426	11	IV A	Refitted, coarse, undecorated	111	C_{14}-C_{30}	-	-	-	-28.3	-33.0	-4.6	Dairy fats
SIE-C-5427	11	IV A	Single, coarse, undecorated	89	C_{14}-C_{30}*	C_{24}-C_{32}	C_{31}-C_{33}	-	-	-	-	*nd*
SIE-C-5428	11	IV A	Single, coarse, undecorated	1314	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-26.6	-28.0	-1.4	Mixture ruminant and non-ruminant adipose fats
SIE-C-5429	11	IV A	Single, coarse, undecorated	3	-	-	-	-	-	-	-	-
SIE-C-5430	4	IV B	Refitted, coarse, undecorated	626	C_{14}-C_{30}	C_{16}-C_{18}	-	-	-27.7	-31.3	-3.5	Mixture dairy and non-ruminant adipose fats
SIE-C-5431	5	IV B	Single, coarse, undecorated	3304	C_{14}-C_{26}	C_{18}	-	-	-28.3	-31.3	-2.9	Mixture ruminant and non-ruminant adipose fats
SIE-C-5432	5	IV B	Single, coarse, undecorated	629	C_{14}-C_{26}	C_{16}-C_{26}	-	-	-26.4	-26.7	-0.3	Mixture ruminant and non-ruminant adipose fats
SIE-C-5433	20	IV B	Single, coarse, undecorated	9	-	-	-	-	-	-	-	*nd*
SIE-C-5434	20	IV B	Single, coarse, undecorated	2	-	-	-	-	-	-	-	-
SIE-C-5435	20	IV B	Single, fine, undecorated	7	-	-	-	-	-	-	-	*nd*
SIE-C-5436	20	IV B	Single, fine, undecorated	27	-	-	-	-	-	-	-	*nd*
SIE-C-5437	20	IV B	Single, coarse, undecorated	52	C_{14}-C_{30}	C_{16}-C_{30}	-	-	-29.2	-32.3	-3.1	Ruminant adipose fats
SIE-C-5438	20	IV B	Single, coarse, undecorated	82	C_{14}-C_{28}	C_{16}-C_{18}	-	-	-29.1	-32.2	-3.1	Ruminant adipose fats
SIE-C-5439	20	IV B	Refitted, coarse, undecorated	7	-	-	-	-	*nd*	*nd*	*nd*	Animal fats
SIE-C-5440	20	IV B	Single, coarse, undecorated	19	-	-	-	-	-	-	-	*nd*
SIE-C-5441	20	IV B	Single, fine, undecorated	12	-	-	-	-	-	-	-	*nd*
SIE-C-5442	20	IV B	Single, fine, undecorated	22	C_{14}-C_{26}	C_{16}-C_{18}	-	-	-	-	-	*nd*
SIE-C-5443	22	IV B	Single, coarse, undecorated	481	C_{14}-C_{28}	C_{16}-C_{18}	-	-	-28.7	-31.5	-2.8	Mixture ruminant and non-ruminant adipose fats

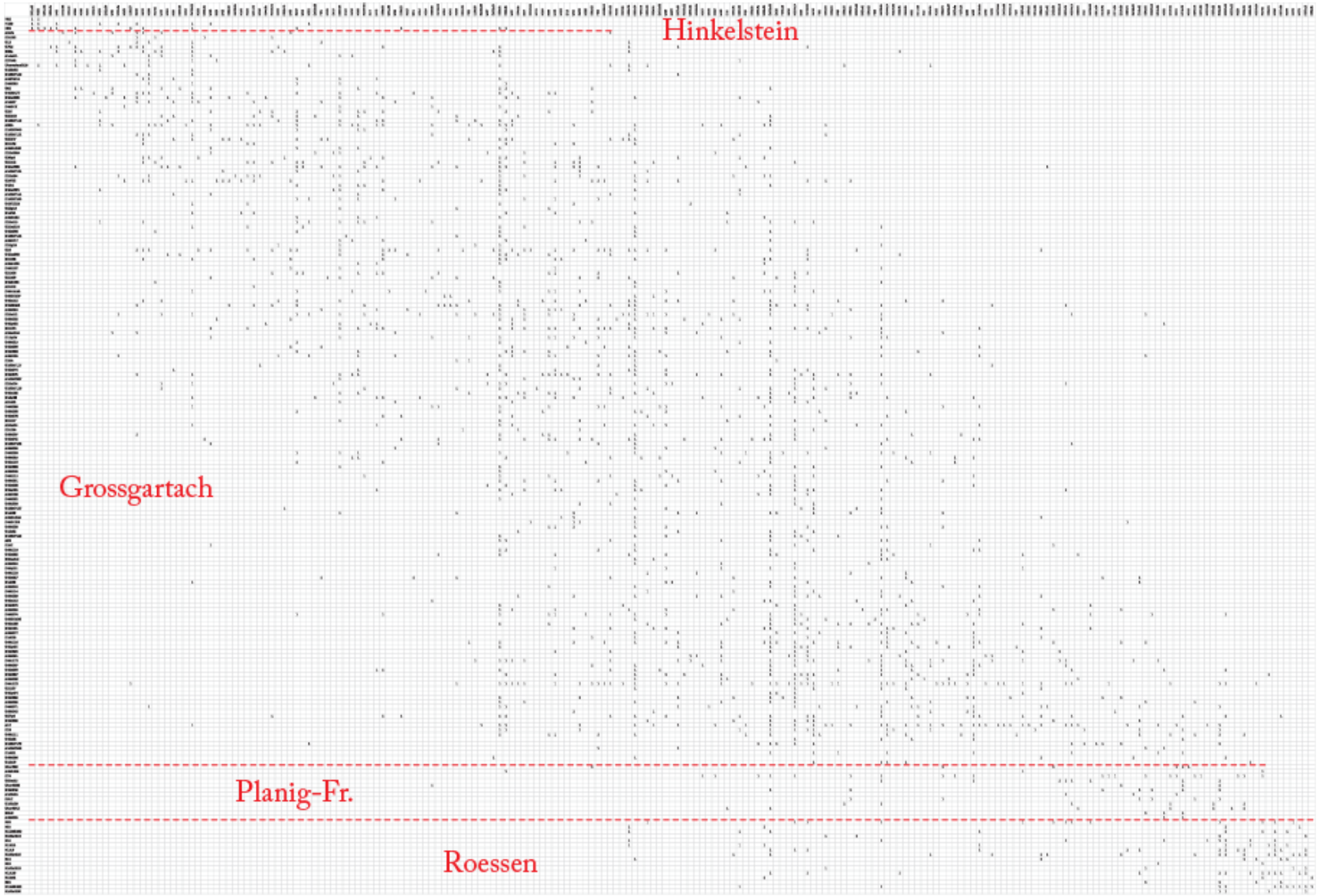
Appendix 6-17: LBK ceramics in lower Alsace: sorted and phased matrix of the correspondence analysis of. Courtesy of A. Bayliss and A. Denaire.



Appendix 6-18: Radiocarbon dates available for the LBK site of Bischoffsheim "AFUA du Stade", LBK site of Rosheim "Rittergass" and Middle Neolithic site of Rosheim "Rosenmeer". Adapted from Denaire *et al.* (2017, Table 1 and Table 2).

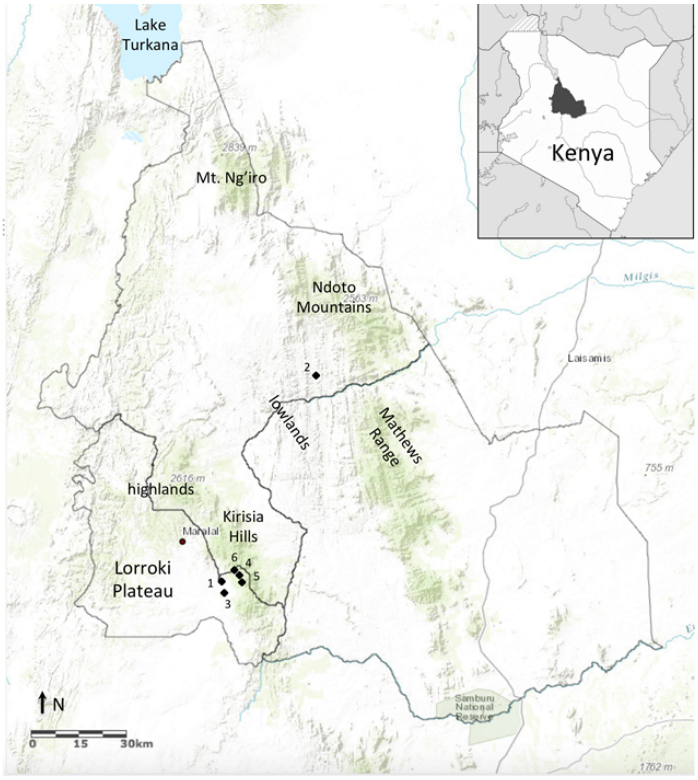
Laboratory #	Site	Phase	Pit, Square	Age ± 1σ (BP)	Calendar age (95% prob.)
SUERC-47710	BIS	LBK IIB	1413	6,257 ± 33	5,316 – 5,078 BC
OxA-29695	BIS	LBK IIB	264, A14	6,225 ± 40	5,304 – 5,058 BC
SUERC-55324	BIS	LBK IIB	696	6,207 ± 34	5,292 – 5,055 BC
SUERC-46497	BIS	LBK IIC	215	6,288 ± 34	5,328 – 5,211 BC
OxA-27805	BIS	LBK IIC	430	6,281 ± 31	5,316 – 5,215 BC
OxA-28981	BIS	LBK IIC	1	6,209 ± 33	5,294 – 5,056 BC
SUERC-47711	BIS	LBK IIC	1961	6,206 ± 33	5,292 – 5,054 BC
OxA-27768	BIS	LBK III	138	6,205 ± 32	5,291 – 5,054 BC
SUERC-46452	BIS	LBK III	1682	6,192 ± 33	5,288 – 5,063 BC
OxA-X-2555-56	BIS	LBK III	138, A20	6,270 ± 90	5,467 – 5,011 BC
OxA-29630	BIS	LBK III	138, B15	6,219 ± 33	5,300 – 5,061 BC
OxA-30786	BIS	LBK III	1403, 1	6,252 ± 38	5,315 – 5,074 BC
SUERC-55326	BIS	LBK III	1403, 5	6,224 ± 34	5,302 – 5,196- BC
OxA-27772	BIS	LBK IVa1	1735	6,161 ± 36	5,215 – 5,008 BC
OxA-27773	BIS	LBK IVa1	1807	6,219 ± 36	5,300 – 5,058 BC
SUERC-46499	BIS	LBK IVa1	1807	6,337 ± 34	5,462 – 5,220 BC
SUERC-46498	BIS	LBK IVa2	1201	6,219 ± 34	5,300 – 5,060 BC
SUERC-46509	BIS	LBK IVb	940	6,084 ± 34	5,206 – 4,851 BC
OxA-27776	BIS	LBK IVb	941	6,172 ± 32	5,218 – 5,028 BC
SUERC-46510	BIS	LBK IVb	941	6,156 ± 34	5,212 – 5,010 BC
SUERC-46511	ROS	LBK IVb	3011	6,183 ± 34	5,226 – 5,020 BC
OxA-27807	ROS	LBK IVb	3011	6,202 ± 30	5,290 – 5,055 BC
SUERC-46512	ROS	LBK IVb	3039	6,174 ± 34	5,220 – 5,020 BC
OxA-27808	ROS	LBK IVb	3039	6,222 ± 31	5,300 – 5,064 BC
SUERC-46513	ROS	LBK IVb	3034	6,185 ± 34	5,281 – 5,026 BC
OxA-27809	ROS	LBK IVb	3034	6,274 ± 31	5,317 – 5,212 BC
SUERC-46274	ROS	Grossgartach	85	5,839 ± 33	4,735 – 4,645 BC
SUERC-46275	ROS	Grossgartach	76	5,767 ± 31	4,720 – 4,640 BC
OxA-27812	ROS	Grossgartach	76	5,865 ± 31	
SUERC-46276	ROS	Grossgartach	89	5,732 ± 33	4,705 – 4,635 BC
OxA-27813	ROS	Grossgartach	112	5,845 ± 33	4,745 – 4,655 BC
OxA-27814	ROS	Grossgartach	45	5,833 ± 29	4,730 – 4,655 BC
SUERC-46277	ROS	Grossgartach	45	5,830 ± 33	
SUERC-46278	ROS	Grossgartach	108	5,787 ± 33	4,720 – 4,635 BC
OxA-27815	ROS	Grossgartach	91	5,812 ± 30	4,730 – 4,645 BC
SUERC-46279	ROS	Grossgartach	88	5,792 ± 33	4,720 – 4,635 BC
OxA-27816	ROS	Grossgartach	83	5,898 ± 29	4,750 – 4,690 BC
SUERC-46283	ROS	Grossgartach	100	5,789 ± 33	4,720 – 4,635 BC
OxA-27817	ROS	Grossgartach	95	5,847 ± 30	4,745 – 4,660 BC
SUERC-46284	ROS	Grossgartach	111	5,791 ± 33	4,720 – 4,635 BC
OxA-27818	ROS	Grossgartach	87	5,885 ± 31	4,750 – 4,685 BC
SUERC-46435	ROS	Grossgartach	82	5,816 ± 28	4,725 – 4,640 BC
SUERC-46443	ROS	Roessen	36	5,753 ± 33	4,635 – 4,500 BC
OxA-27972	ROS	Roessen	50	5,772 ± 35	
OxA-27973	ROS	Roessen	50	5,803 ± 32	4,640 – 4,540 BC
SUERC-46444	ROS	Roessen	50	5,735 ± 32	
OxA-27822	ROS	Roessen	55	5,804 ± 30	4,645 – 4,540 BC
SUERC-46445	ROS	Roessen	55	5,731 ± 30	

Appendix 6-19: Middle Neolithic ceramics assemblages in Lower Alsace: sorted and phased matrix of the correspondence analysis. Courtesy of A. Bayliss and A. Denaire.

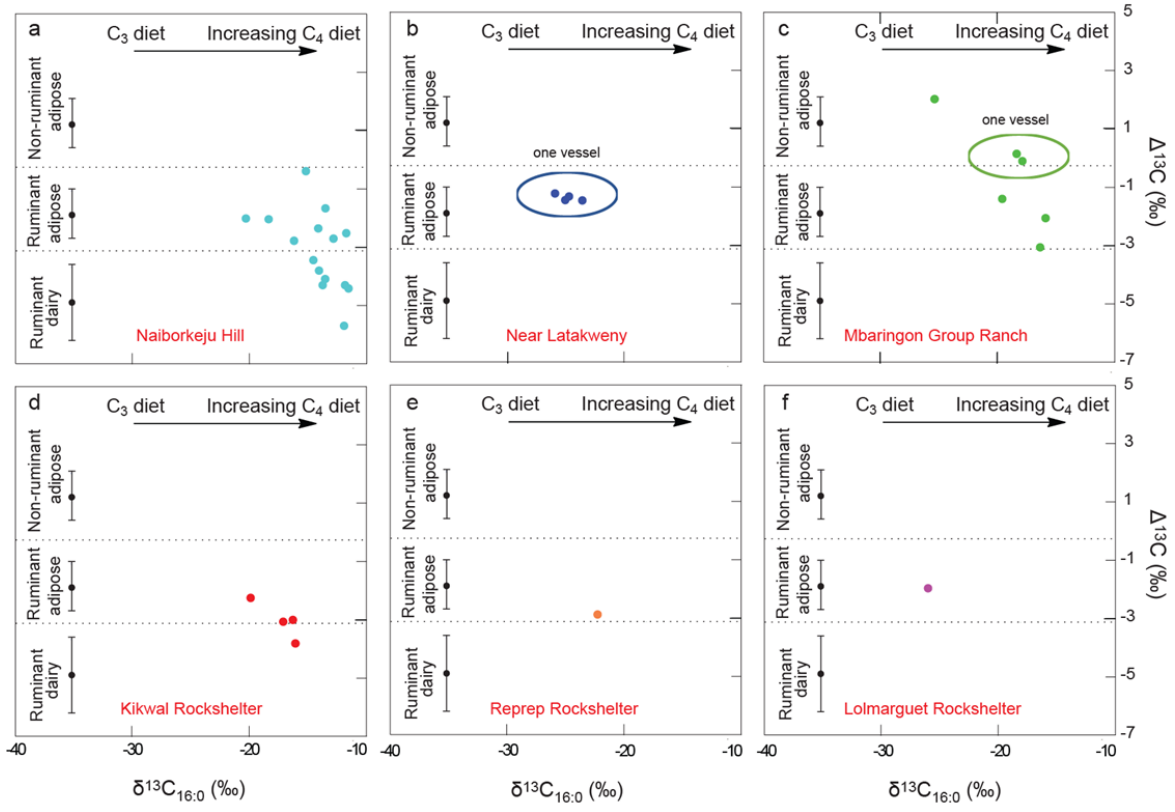


Appendix 7: Dairy residues: Samburu, Kenya and LBK, Europe

Appendix 7-1: Map of Samburu County, Kenya. From Dunne *et al.* (In press, Figure 1).



Appendix 7-2: (a-f) $\Delta^{13}C$ values from the Samburu potsherds by site. From Dunne *et al.* (In press, Figure 4).

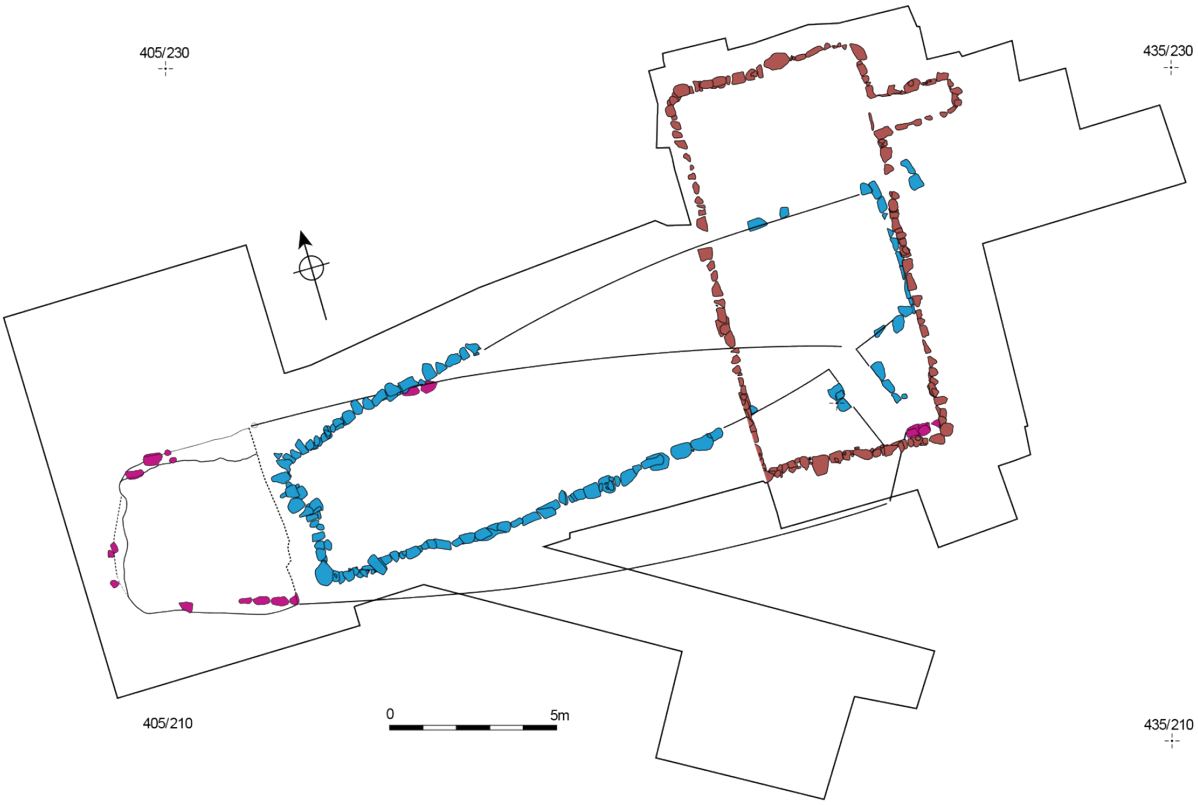


Appendix 7-3: Details of lipid residue analysis of pottery vessels sampled for the radiocarbon dating of dairying residues. Unpublished data from the NeoMilk database.

Site	Country	Sherd #	LBK Phase	Context	Potsherd	C ($\mu g.g^{-1}$)	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
Apc-Berekalja I	Hungary	APC-C-4217	-	697	Single, coarse, undecorated	653	-26.6	-31.0	-4.4	Dairy fats
		APC-C-4200	-	589	Single, coarse, undecorated	590	-26.4	-31.1	-4.7	Dairy fats
Bischoffsheim	France	BIS-C-4519	Late IVa1	538	Single, coarse, undecorated	1435	-24.5	-23.6	0.9	Non-ruminant adipose fats
		BIS-C-4527	Late IVa1	538	Single, coarse, undecorated	2477	-30.9	-35.0	-4.1	Dairy fats
		BIS-C-4529	Late IVa1	538	Single, coarse, undecorated	2022	-25.9	-26.6	-0.7	Ruminant adipose fats
		BIS-C-4531	Late IVa1	538	Single, coarse, undecorated	974	-24.9	-24.6	0.3	Non-ruminant adipose fats
Cuiry-les-Chaudardes	France	CUI-C-5708	Late I	25	Single, coarse, undecorated	881	-26.6	-32.5	-5.9	Dairy fats
		CUI-C-5776	Late II	378	Single, coarse, undecorated	3532	-30.2	-33.6	-3.4	Dairy fats
		CUI-C-5801	Late II	386	Single, coarse, undecorated	9886	-28.2	-33.3	-5.0	Dairy fats
		CUI-C-5735	Late III	241	Single, coarse, undecorated	3417	-29.1	-33.9	-4.8	Dairy fats
Ensisheim	France	ENS-C-5913	Early II	9	Single, coarse, undecorated	1177	-27.3	-30.9	-3.6	Dairy fats
		ENS-C-5915	Early II	9	Single, coarse, undecorated	771	-26.4	-29.6	-3.2	Dairy fats
		ENS-C-5934	Early II	28	Single, coarse, undecorated	1647	-26.2	-29.7	-3.5	Dairy fats
		ENS-C-5940	Early II	28	Single, coarse, undecorated	2082	-28.7	-30.9	-2.2	Ruminant adipose fats
Geleen-Janskamperveld	Netherland	GEL-C-3271	Ib	49015	Single, coarse, undecorated	1260	-30.4	-33.5	-3.1	Dairy fats
		GEL-C-3276	Ib	49015	Single, coarse, undecorated	339	-31.8	-35.2	-3.4	Dairy fats
		GEL-C-3298	II	49016	Single, coarse, undecorated	577	-29.0	-31.8	-2.8	Ruminant adipose fats
		GEL-C-3299	II	49016	Single, coarse, undecorated	2743	-30.0	-33.1	-3.1	Dairy fats
Karwowo 1	Poland	KAR-C-3636	-	43	Single, coarse, undecorated	3316	-26.0	-26.9	-0.9	Non-ruminant adipose fats
		KAR-C-3677	-	43	Refitted, coarse, undecorated	1900	-26.5	-30.7	-4.3	Dairy fats
Konigshoven 14	Germany	KON-C-5594	Early	522	Single, coarse, undecorated	531	-32.0	-34.4	-2.4	Ruminant adipose fats
		KON-C-5598	Early	522	Single, coarse, undecorated	1023	-31.0	-35.1	-4.1	Dairy fats
		KON-C-5617	Early	522	Single, coarse, undecorated	678	-28.5	-31.9	-3.4	Dairy fats
Kopydlowo	Poland	KOP-C-2949	-	25 B	Refitted, fine, undecorated	548	-25.5	-29.4	-3.9	Dairy fats
Ludwinowo 7	Poland	LDW-C-2267	IIB	A49	Single, coarse, undecorated	323	-26.6	-29.2	-2.6	Dairy fats
		LDW-C-2272	IIB	A50	Single, coarse, undecorated	1628	-25.7	-29.7	-4.0	Dairy fats
Maastricht-Klinkers	Netherland	MAK-C-3094	IIb	207	Single, coarse, undecorated	494	-29.0	-32.4	-3.4	Dairy fats
		MAK-C-3099	IIb	207	Single, coarse, undecorated	7672	-27.8	-27.5	0.4	Non-ruminant adipose fats

Appendix 8: Bornais, South Uist, Scotland

Appendix 8-1: Excavation at Mound 2 with floor plans of house1 (purple), house 2 (blue) and house 3 (red). Courtesy of N. Sharples.



Appendix 8-2: Results of lipid residue analysis of potsherds from the site of Bornais Mound 2, House 2. The sample with *V* corresponds to the visible residues. P corresponds to the Phytanic acid and TMDT to the 4,8,12-trimethyltridecanoic acid.

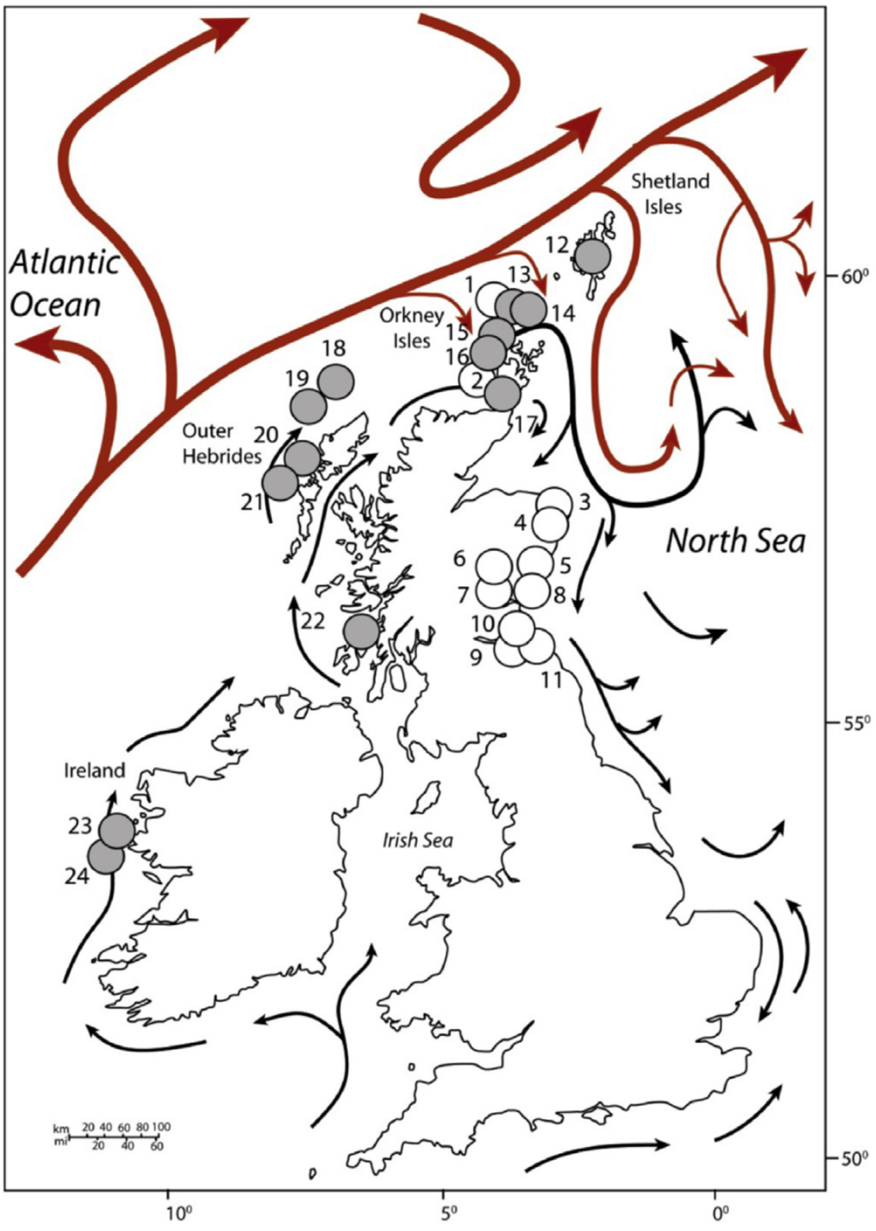
Sherd #	Block	Code	Potsherd	C ($\mu g.g^{-1}$)	FAs	DHYAs	APAAs	IFAs	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BN-132	BCA	1259/3790	Refitted	849	C_{14}-C_{18}	-	-	(TMTD), P	-25.8	-31.0	-5.2	Mixture dairy fats
BN-133	BCA	1280/9448/3/3887	Refitted	137	C_{14}-C_{18}	C_{18}	-	-	-	-	-	*nd*
BN-134	BCB	6/8656	Single	190	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	-	-	-	*nd*
BN-135	BCB	1089/8654	Single	1444	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	-	(TMTD), P	-26.3	-26.6	-0.2	Mixture ruminant adipose, marine fats
BN-136	BCB/C	1074/2/3529	Refitted	207	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	-	-26.7	-32.9	-6.2	Mixture dairy, marine fats
BN-137	BCC	182/1/8659	Single	676	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	-24.9	-28.4	-3.5	Mixture dairy, marine fats
BN-138	BCC	528/2199	Single	19	C_{14}-C_{22}	-	-	-	-	-	-	*nd*
BN-139	BCC	549/2264	Refitted	3135	C_{14}-C_{20}	C_{18}, C_{22}	C_{18}	-	-26.6	-29.3	-2.7	-
BN-139V	*BCC*	*549/2264*	-	*3064*	*C_{16}-C_{22}*	*C_{18}*	*C_{18}, (C_{20})*	*P*	-	-	-	*nd*
BN-140	BCC	550/5/2458	Single	216	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, C_{20}, C_{22}	TMTD, P	-22.1	-25.2	-3.1	Marine fats
BN-141	BCC	550/5/2458	Single	28	C_{16}-C_{22}	(C_{18})	-	-	-26.6	-32.5	-5.9	Mixture dairy, non-ruminant fats
BN-142	BCC	557/5/2341	Single	2220	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20})	(TMTD), P	-24.9	-27.9	-3.0	-
BN-142V	*BCC*	*557/5/2341*	-	*100*	*C_{18}-C_{22}*	-	-	-	-	-	-	*nd*
BN-143	BCC	557/5/8660	Refitted	5630	C_{14}-C_{20}	C_{18}	C_{18}	P	-25.8	-27.9	-2.2	Mixture ruminant adipose fats
BN-144	BCC	558/5/8670	Single	2483	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	(TMTD), P	-25.6	-28.9	-3.3	Mixture dairy, marine fats
BN-145	BCC	565/8655	Refitted	1425	C_{14}-C_{22}	C_{18}	-	P	-27.0	-31.3	-4.3	Mixture dairy, non-ruminant fats
BN-146	BCC	921/2992	Single	1349	C_{14}-C_{22}	C_{18}	C_{18}	P	-25.6	-30.2	-4.6	Mixture dairy, non-ruminant fats
BN-147	BCC	1008/3063	Single	56	C_{16}-C_{22}	(C_{18})	-	-	-	-	-	*nd*
BN-147V	*BCC*	*1008/3063*	-	*13*	-	-	-	-	-	-	-	*nd*
BN-148	BCC	1008/9452/8657	Single	60	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20}, C_{22})	TMTD, P	-25.3	-29.2	-4.0	Mixture dairy, marine fats
BN-149	BCC	1010/9685/2/3279	Refitted	3984	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	(TMTD), P	-26.3	-30.4	-4.1	Mixture dairy, marine fats
BN-149V	*BCC*	*1010/9685/2/3279*	-	*3385*	*C_{16}-C_{22}*	*C_{18}, C_{20}, C_{22}*	*C_{18}, C_{20}, C_{22}*	*TMTD, P*	*-25.1*	*-29.3*	*-4.3*	Mixture dairy, marine fats
BN-150	BCC	1010/2/3266	Single	1460	C_{14}-C_{22}	C_{18}, (C_{20}, C_{22})	C_{18}, C_{20}, C_{22}	TMTD, P	-25.2	-29.0	-3.8	Mixture dairy, marine fats
BN-151	BCC	1049/9809/8661	Refitted	2141	C_{14}-C_{22}	C_{18}, (C_{20}, C_{22})	C_{18}	P	-26.9	-29.6	-2.7	Mixture ruminant adipose fats
BN-152	BCC	1057/9895/8656	Single	0	-	-	-	-	-	-	-	-
BN-153	BCC	1057/9894/3522	Refitted	1409	C_{14}-C_{22}	(C_{18})	C_{18}	-	-26.5	-29.8	-3.3	Mixture dairy, non-ruminant fats
BN-154	BCC	1057/9893/3461	Refitted	1153	C_{14}-C_{20}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20}, C_{22})	TMTD, P	-27.0	-30.1	-3.0	Mixture ruminant adipose, marine fats
BN-155	BCC	1057/9894/3535	Refitted	4198	C_{14}-C_{22}	-	-	-	-26.5	-28.6	-2.2	Mixture ruminant adipose fats
BN-156	BCC	1057/9894/8666	Single	276	C_{14}-C_{18}	-	-	-	-25.3	-28.9	-3.6	Mixture dairy, non-ruminant fats
BN-157	BCC	1079/2/8671	Refitted	11	C_{16}-C_{22}	C_{18}	-	TMTD, P	-	-	-	*nd*
BN-158	BCC	1220/9991/3662	Refitted	12	-	(C_{18})	-		-	-	-	*nd*
BN-159	BCC	1220/9991/8664	Refitted	1178	C_{14}-C_{20}	C_{18}	C_{18}	P	-26.4	-32.0	-5.6	Mixture dairy, non-ruminant fats
BN-160	BCC	1234/9492/8665	Refitted	4559	C_{14}-C_{22}	C_{18}	C_{18}	(TMTD), P	-26.4	-31.0	-4.6	Mixture dairy, non-ruminant fats
BN-160V	*BCC*	*1234/9492/8665*	-	*2371*	*C_{16}-C_{18}*	*C_{18}*	*C_{18}, (C_{20})*	*P*	*-26.6*	*-31.9*	*-5.2*	Mixture dairy, non-ruminant fats
BN-161	BCC	1260/9467/3779	Single	546	C_{14}-C_{18}	(C_{18}, C_{20}, C_{22})	-	-	-25.7	-31.2	-5.5	Mixture dairy, non-ruminant fats
BN-162	BCC	1260/9465/8672	Single	1574	C_{16}, C_{18}	(C_{18})	-		-26.7	-29.3	-2.6	Mixture ruminant adipose fats
BN-163	BCC	2192/11902/10/2192	Refitted	452	C_{14}-C_{18}	C_{18}	C_{18}	-	-27.3	-31.5	-4.2	Mixture dairy, non-ruminant fats
BN-164	BCC	2225/11943/6230	Refitted	129	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}	TMTD, P	-25.8	-31.6	-5.8	Mixture dairy, marine fats

Sherd #	Block	Code	Potsherd	C (µg.g^{-1})	FAs	DHYAs	APAAs	IFAs	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BN-165	BCC	2231/11968/14/6214	Single	1823	C_{14}-C_{18}	(C_{18})	-	-	-26.3	-30.1	-3.7	Mixture dairy, non-ruminant fats
BN-166	BCC	2258/11287/15/8663	Refitted	246	C_{16}, C_{18}	C_{18}	C_{18}, C_{20}	TMTD, P	-25.8	-31.7	-5.9	Mixture dairy, marine fats
BN-167	BCC	2264/6314	Single	946	C_{14}-C_{22}	(C_{18}, C_{20}, C_{22})	C_{18}, C_{20}, C_{22}	TMTD, P	-23.5	-26.6	-3.1	Marine fats
BN-167V	*BCC*	*2264/6314*	-	*3633*	*C_{16}-C_{20}*	-	*C_{18}, C_{20}, (C_{22})*	*P*	*-26.3*	*-31.5*	*-5.2*	Mixture dairy, marine fats
BN-168	BCC	2264/14/6312	Refitted	1105	C_{16}, C_{18}	C_{18}	C_{18}	-	-29.2	-31.5	-2.3	Ruminant adipose fats
BN-169	BCC	2264/14/8667	Refitted	2	C_{18}, C_{22}	-	-	-	-	-	-	-
BN-170	BCC	2285/11278/19/8662	Refitted	4231	C_{14}-C_{22}	-	C_{18}, C_{20}, C_{22}	TMTD, P	nd	nd	nd	Marine fats
BN-171	BCC	2297/11318/19/8658	Refitted	872	C_{14}-C_{22}	C_{18}	C_{18}	P	-26.2	-32.2	-6.0	Mixture dairy, non-ruminant fats
BN-172	BCC	2613/9/6398	Refitted	834	C_{16}-C_{20}	(C_{18}, C_{20})	C_{18}	P	-26.1	-28.5	-2.4	Mixture ruminant adipose fats
BN-173	BCC	2637/11398/6500	Single	2376	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, C_{20}, C_{22}	TMTD, P	-26.0	-30.5	-4.5	Mixture dairy, marine fats
BN-174	BCC	2657/11464/16/6523	Single	1176	C_{14}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20}, C_{22})	(TMTD), P	-25.9	-28.5	-2.6	-
BN174V	*BCC*	*2657/11464/16/6523*	Single	*5724*	*C_{16}-C_{22}*	*(C_{18}), C_{22}*	*C_{18}, C_{20}, C_{22}*	*TMTD, P*	*-26.3*	*-30.0*	*-3.7*	Mixture dairy, marine fats
BN-175	BCC	2673/11489/13/8669	Single	41	C_{16}-C_{22}	C_{18}, (C_{22})	C_{18}, C_{20}, C_{22}	(TMTD), P	-25.6	-29.8	-4.2	Mixture dairy, marine fats
BN-176	BCC	2692/12041/7300	Single	924	C_{16}-C_{20}	C_{18}, (C_{20}, C_{22})	C_{18}, (C_{20}, C_{22})	P	-26.4	-29.0	-2.6	Mixture ruminant adipose fats
BN176V	*BCC*	*2692/12041/7300*	Single	*2225*	*C_{16}-C_{22}*	-	*C_{18}, C_{20}, C_{22}*	*TMTD, P*	*-27.0*	*-30.9*	*-3.9*	Mixture dairy, marine fats
BN-177	BCC	2700/12057/6631	Single	497	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, (C_{20})	TMTD, P	-25.1	-30.3	-5.2	Mixture dairy, marine fats
BN-178	BCC	2715/12090/20/6637	Single	280	C_{16}-C_{22}	C_{18}, C_{20}, C_{22}	C_{18}, C_{20}, (C_{22})	TMTD, P	-	-	-	-
BN178V	*BCC*	*2715/12090/20/6637*	Single	*2298*	*C_{16}-C_{22}*	*(C_{18}, C_{20}, C_{22})*	*C_{18}, C_{20}, C_{22}*	*TMTD, P*	*-24.1*	*-27.7*	*-3.6*	Mixture dairy, marine fats
BN-179	BCC	2731/1204/20/6686	Single	1083	C_{14}-C_{20}	(C_{18})	C_{18}	P	-26.5	-29.8	-3.2	Mixture dairy, non-ruminant fats
BN-180	BCC	545+39/2501	Refitted	536	C_{16}-C_{20}	(C_{18})	C_{18}, C_{20}, C_{22}	P	-24.4	-28.1	-3.7	Mixture dairy, marine fats

Appendix 8-3: Details of lipid residue analysis of pottery vessels previously analysed and sampled for radiocarbon dating of lipid residues (Cramp forthcoming).

Sherd #	Block	Code	Phase	Potsherd	C (µg.g^{-1})	Aquatic biomarkers	$\delta^{13}C_{16:0}$ (‰)	$\delta^{13}C_{18:0}$ (‰)	$\Delta^{13}C$ (‰)	Assignment
BN-74	BAC	1913/5470	LIA2	Refitted	288	APAAs	-26.6	-29.4	-2.8	Ruminant adipose, marine fats (tentative)
BN-89	BAC	1917/5681	LIA2	Single	163	-	-26.8	-29.4	-2.5	Ruminant adipose fats
BN-87	BAF	2626/6719/11378	LIA2	Single	246	APAAs	-26.8	-30.4	-3.6	Ruminant adipose, marine fats (tentative)
BN-77	BAF	2626/6719/11378	LIA2	Refitted	296	-	-26.9	-29.9	-3	Ruminant adipose fats
BN-88	BAG	1075/8588	EN/LIA2	Single	160	APAAs, DHFAs	-24.2	-25.4	-1.3	Ruminant adipose, marine fats
BN-110	BBA	1909/8609	EN	Single	85	APAAs	-25.4	-25.9	-0.5	Marine fats
BN-35	BBD	43/1635	EN	Refitted	98	APAAs, DHFAs	-25.4	-31.4	-6	Ruminant adipose, marine fats
BN-91	BBD	1257/8617/9471	EN	Single	123	APAAs, DHFAs	-24.3	-27.9	-3.6	Ruminant adipose, marine fats
BN-101	BBD	44/8614	EN	Single	111	-	-28.1	-32.2	-4.1	Dairy fats
BN-105	BBD	43/8612	EN	Single	225	-	-26.2	-31.7	-5.4	Dairy fats
BN-115	BCA	1239/4178/9483	MN	Refitted	171	-	-27.2	-31	-3.8	Dairy fats
BN-38	AD	69/1638	MN	Single	85	APAAs	-25.7	-29.4	-3.7	Dairy, marine fats (tentative)
BN-36	AG	58/1636	LN	Single	59	APAAs, DHFAs	-27.3	-31.8	-4.5	Dairy, marine fats
BN-131	GDC	1637/5305	LN	Single	140	-	-26.8	-30.8	-4	Dairy fats

Appendix 8-4: Modern water circulation of the Atlantic water (red arrows) and coastal currents around the British Isles (black arrows). The dots represent all the sites studied for the MRE. From Russell *et al.* (2015, Figure 2).



1: Quoygrew
2: Robert's Haven
3: Gallowgate
4: 16-18 Netherkirkgate
5: Arbroath Abbey
6: Horsecross
7: Kirkgate
8: St. Leonard's School
9: Archerfield
10: Scottish Seabird Centre
11: Castle Park
12: Scatness
13: St. Boniface
14: Lopness
15: Galson
16: Skara Brae
17: Freswick Links
18: Birsay Bay
19: Berie
20: Baleshare
21: Hornish Point
22: Carding Mill Bay
23: Omey island
24: Doonloughan